THE UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

EFFECT OF OPERATING VARIABLES ON HYDROGENATION OF COTTONSEED OIL

A THESIS

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

DOCTOR OF PHILOSOPHY

BY

IBRAHIM ABDALLA ELDIB

Norman, Oklahoma

1955

EFFECT OF OPERATING VARIABLES ON HYDROGENATION OF COTTONSEED OIL

BY

Lyle F. Albright

R L Huntington

Alfred Clatenous

[illegible]

P. J. Pickard

THESIS COMMITTEE

To my wife Wilma, through whose patience,
encouragement, and cooperation I have
been able to complete this work.

ACKNOWLEDGMENT

The author wishes to express his appreciation to all who aided in this investigation and especially to:

Professor L. F. Albright, who supervised this work, for his guidance, encouragement, and help throughout the course of this project.

Professors Alfred Chatenever, Bruce Houston, and R. L. Huntington for their interest in the project and constructive criticism.

Professor P. L. Pickard and Mr. G. W. Polly for their assistance in the instrumental analysis.

Mr. John Fox for his aid in the construction of the equipment.

The Texas Company, under whose fellowship this research was conducted.

Mrs. Tucker's Co., Inc., a division of Anderson Clayton, Inc., for supplying the cottonseed oil used in the project.

Harshaw Chemical Co. for supplying the nickel catalyst.

Drs. E. A. Lawrence and Harold Crosier of Colgate-Palmolive-Peet Co. for their suggestions and advice.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF ILLUSTRATIONS

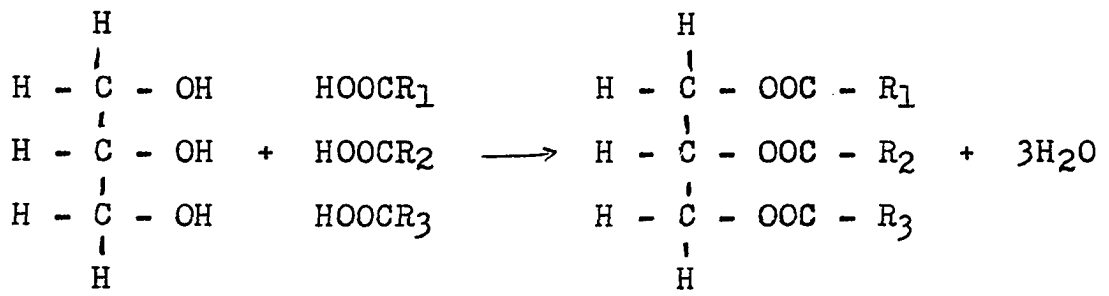
EFFECT OF OPERATING VARIABLES ON HYDROGENATION OF COTTONSEED OIL

CHAPTER I

INTRODUCTION

The rapid advance of the oil and fat technology in the past few years has encouraged ever increasing fundamental research.[1] Hydrogenation as one of the most important phases of this industry has long been performed by methods developed primarily by empirical means. Significant improvements of commercial hydrogenation probably could be possible if the basic fundamentals of the hydrogenation reaction were better understood.

Naturally occurring vegetable and animal fats or oils consist predominantly of triglycerides. These can be considered to be formed by the condensation of one molecule of glycerine with three of fatty acids to yield one molecule of triglyceride and three of water. This hypothetical reaction is illustrated as follows:



R_1, R_2 and R_3 are straight chain hydrocarbon radicals containing 7 to 21 carbon atoms, and they make up a greater portion of the triglyceride molecule. Triglycerides found in nature always have some fatty acid radicals that contain ethylenic double bonds. These double bonds are frequently the most reactive portions of the molecules. Both the chemical and physical properties of the oils and fats are largely determined by the fatty acids that they contain. The number of ethylenic double bonds found in a fatty acid radical may be as high as four or more. The length of the fatty acid radicals and the degree of unsaturation vary significantly with the source of the oil. Ethylenic double bonds of naturally occurring fatty acids are almost exclusively in the cis form. Those fats with high degrees of unsaturation and/or with short fatty acid chains tend to occur in the liquid state.

Vegetable or animal fats and oils all contain small amounts of various substances other than triglycerides.[1] Some of these substances are partially or completely recovered from the crude oils during refining and hence do not

appear in most manufactured products. Among these substances are phosphatides, carbohydrates, and certain protein degradation products. Of those substances which remain through refining, some are without pronounced flavor, odor or color, such as sterols and fatty alcohols. These are relatively inert from a chemical standpoint, and their presence is neither objectionable nor desirable, insofar as most of the uses of the oils are concerned. However, certain other compounds may affect the character of the oil considerably, even though they are present only in traces. The characteristic yellow-red color of most fats and oils is attributed to cartenoid pigments; structurally, the cartenoids consist of highly unsaturated hydrocarbon chains, or isoprene units arranged in various cyclic and acyclic configurations. The superior resistance to oxidative deterioration of natural fats and oils over pure triglycerides is due to their content of antioxidants such as tochopherols and gossypol. The characteristic flavors and odors of fats and oils have been explained essentially by their content of high molecular weight ketones. Fats and oils also contain components of nutritional significance, such as fat soluble vitamins A, D and E. Fats and oils may contain, even after refining, traces of phosphorous from the presence of residual phosphatides, and traces of sodium soaps left from the alkali refining process.

The earliest work done on hydrogenation was conducted in the period from 1897 to 1905.[1] Sabatier successfully hydrogenated unsaturated organic substances in the vapor phase without undue side reactions. In 1903, Norman[2] patented a process for the liquid phase hydrogenation of fatty acids. The title to the Norman patent was then passed to the British firm of Crossfield and Sons. In 1909, the Proctor and Gamble Company acquired the rights to the Crossfield patents. In 1911, it placed its hydrogenated cottonseed oil shortening, Crisco, on the market. The marketing of Crisco was so successful that other American manufacturers became interested. Later the Burchenal patent[3] under whose claims the Proctor and Gamble shortening was manufactured was invalidated by a court decision, and the market became open for the manufacture of comparable products by similar processes.

The present state of hydrogenation techniques has been discussed by Bailey.[1] The liquid oil to be hydrogenated is contacted with hydrogen gas in the presence of a catalyst. Catalysts used commercially consist primarily of nickel, although minor amounts of copper, aluminum, etc., may be incorporated with the nickel to act as promoters. Powdered catalysts are normally used, at least in this country, but massive catalysts are reportedly used in Europe and Great Britain.

Catalysts are prepared by special and often highly secret methods. The metals are frequently supported on highly porous, inert, and refractory materials such as Kieselguhr. Although the catalysts decrease in activity with use, deactivation is slow, in most cases, and a single charge of catalyst can be used a number of times.

Operating conditions for commercial hydrogenation vary appreciably with the oil being hydrogenated and the final desired product. The range of conditions normally found in practice are as follows:

Temperature - 100 to 185°C
Hydrogen pressure - atmospheric to 120 psia.
Amount of catalyst - 0.03 to 0.25 percent

Most of the non-glyceride substances present naturally in fats and oils are undesirable and should be removed.(1) Free fatty acids and phosphatides are detrimental to hydrogenation as they tend to poison the catalyst. Other substances render the oil dark colored, cause it to foam or smoke, or are precipitated when the oil is heated in subsequent processing operations. The most important and generally practiced method of refining is by treating the oil with an aqueous alkali solution such as caustic soda, soda ash, or sodium bicarbonate. Alkali refining results in an almost complete removal of free fatty acids, which are converted into oil insoluble soaps. Other acidic substances likewise combine with the alkali, and there is some removal of impurities from the oil by adsorption on the soap formed in the

operation. Phosphatides, proteins or protein fragments, and gummy or mucilaginous substances also are removed since they become insoluble upon hydration. Bleaching generally follows alkali refining in order to reduce the color of the oil. The most important adsorbents used in bleaching fats and oils are bleaching earth or clays and sometimes a mixture of either one with activated carbon. Following refining and bleaching the oil is sometimes either hydrogenated and then steam deodorized, or deodorized and then hydrogenated.

The hydrogen gas used in the process of hydrogenation must be of very high purity.(1) Gaseous sulphur compounds such as hydrogen sulfide, carbon disulfide, sulphir dioxide, and carbon oxysulfide are poisons for nickel catalysts. These compounds are rapidly adsorbed by nickel catalysts and poison them irreversibly. Besides the sulfur compounds mentioned above, carbon monoxide is a catalyst poison which causes trouble in the hydrogenation of oils and fats. Carbon monoxide is adsorbed more slowly than are the sulfur compounds and poisons the catalyst reversibly.

Most of the present commercial hydrogenation of oils and fats is conducted in batch equipment. According to Bailey(1) a well designed hydrogenation reactor should provide good mixing of the hydrogen and oil; mixing of the catalyst-oil mass is of less importance. The batch hydrogenation plants in this country use essentially either "recirculation" or "dead-end" systems. In the recirculation

process, agitation and dispersion of the hydrogen within the oil are achieved by continuously recycling hydrogen in large volumes through the reactor which contains the oil plus dispersed nickel catalyst. The reactors have capacities up to 40,000 pounds of oil, and are equipped with heating coils. The hydrogen gas is bubbled at approximately atmospheric pressures through a distribution device in the bottom of the reactor and withdrawn from the head space by means of a blower. At the end of a run the hydrogen flow is stopped, and the finished charge is pumped to a filter press where the catalyst is removed. In the dead-end hydrogenator, hydrogen gas is introduced to the oil through sparging rings, but it is not recirculated. The gas bubbles up through the oil and forms a pocket above it. This type of reactor is always provided with a motor-driven agitator, and it is generally operated at pressures significantly above atmospheric. In commercial operations, a portion of the gas in the reactor is vented to remove gas poisons. The dead-end reactor holds up to 40,000 pounds of oil and is designed for working pressures of 100 to 150 psig. Coils are provided within the vessel to maintain suitable temperature control using either steam or water. In both the recirculation and dead-end systems, the catalyst is finely divided nickel impregnated in a fat and is marketed as solid flakes generally containing about 25% nickel by weight.

A continuous hydrogenation process has been

reported[1] in which the catalyst used is nickel turnings enclosed in a cylindrical cage of metal screen. The cages are placed in cylinders, through which the oil is pumped while in an atmosphere of hydrogen. A recent series of patents issued to Mills et al[4] describes a continuous hydrogenation apparatus using powder catalyst. Intensive agitation and relatively high pressures are used to achieve extremely rapid hydrogenation rates.

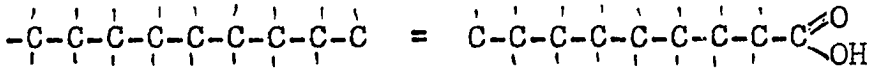
Fats or oils which are hydrogenated in this country in large quantities include cottonseed oil, soyabean oil, linseed oil, peanut oil, lard, and tallows. Most of the hydrogenated products are used in shortenings or oleomargarine, but considerable amounts are also used in the soap industry. The use of hydrogenated fats has progressed until most present day shortenings are completely or almost completely hydrogenated. Advantages of these hydrogenated shortenings as compared to unhydrogenated fats are, better odor and color characteristics, increased age and cooking stability, and more desirable softening and melting temperatures. The estimated world production of cottonseed oil per year is 3,200 million pounds,[5] and a good share of it is hydrogenated.

A typical analysis for the fatty acid radicals of cottonseed oil is as follows:[6]

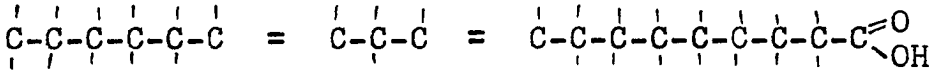
Acid	Formula	% by Weight
Myristic	$C_{14}H_{28}O_2$	0.55
Palmitic	$C_{16}H_{32}O_2$	22.90
Stearic	$C_{18}H_{36}O_2$	2.15
Oleic	$C_{18}H_{34}O_2$	24.70
Linoleic	$C_{18}H_{32}O_2$	49.70

It is noted that all of the unsaturation occurs in the C_{18} acids. The double bond in normally occurring oleic acid is at the 9:10 position and with linoleic acid is at the 9:10 and 12:13 positions. This is shown as follows.

Oleic Acid:



Linoleic Acid:



When cottonseed oil is hydrogenated, the hydrogen can react at the 9:10 or 12:13 position of the linoleic acid or at the 9:10 position of the oleic acid. If the reaction occurs at the 9:10 position of the linoleic acid, an isomer of oleic acid is formed. If hydrogen reacts at the 12:13 position, then an oleic acid is formed. The hydrogenation of oleic acid produces stearic acid. The reactivity of these double bonds varies with operating conditions. If either of the double bonds on the linoleic acid hydrogenates before the 9:10 double bond on the oleic acid, the hydrogenation is

termed selective. Selectivity is then defined as the conversion of linoleic acid to oleic acid preferentially to the conversion of oleic acid to stearic acid. It should be stated, however, that selectivity in actual hydrogenation processes is a relative and not an absolute value.

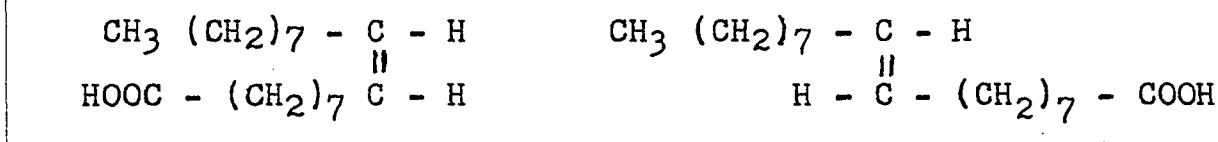
A reliable method for measuring polyunsaturated acids, i.e., linoleic and linolenic, using the ultraviolet spectra was first reported in 1945 by Swain et al.[7] Consequently hydrogenation results dealing with selectivity that were presented prior to that time (Moore et al,[8] Richardson et al,[9,10] Dhingra et al[11] and Bailey[12] and co-workers) may not be completely reliable. This may be verified by some discrepancies in the results concerning the effect of operating variables on selectivity. This is particularly true in regard to the amount of catalyst in the reaction. The results seem to indicate that increased temperature, decreased pressure, or decreased agitation increases selectivity.

In a later investigation, Bailey and Fisher[13] studied the behaviours of the more highly unsaturated acids during hydrogenation. For their investigation they used cottonseed oil, soyabean oil, and linseed oil. They determined the contents of linoleic and linolenic acids using the spectroscopic method of Mitchell, Kraybill, and Zscheile.[14] The percentages of saturated fatty acids were determined by the Bertram method.[1] Their results show that under favorable

conditions for selectivity, the relative reactivities of oleic, linoleic, and linolenic acids are in the ratio of 1:20:40. In a non-selective hydrogenation, it was concluded that the difference in reactivity is much smaller. They found that in the hydrogenation of cottonseed oil the relative reactivities of the oleic acid groups to the linoleic acid groups varied from about 1:5 to 1:23.

The manufacturers of shortening and oleomargarine are very interested in knowing operating conditions that favor selectivity. If the linoleic acid groups are converted into oleic acid groups without the formation of stearic acid, the products obtained will then consist of the glycerides of oleic acid and saturated fatty acids which were originally present in the oil before hydrogenation. Due to the absence of highly unsaturated fatty acids, the products obtained will be characterized by greater stability and at the same time the homogeneity will be improved.

When hydrogenation occurs, some iso-oleic acid is invariably formed. The term iso-oleic acid is generally used to designate the trans-isomer of oleic acids. The oleic acid can itself exist in two forms.



Oleic acid (cis-form)

Elaidic acid (trans-form)

The phenomenon of cis-trans isomerism can be explained[15] by the fact that the inclusion of a double bond in a molecule results in a rigid structure, such that it is impossible for one of the two atoms so joined to rotate with respect to the other. If the two groups attached to each unsaturated carbon atom are different from each other it becomes possible for two different geometrical forms of the molecule to occur. The isomer in which the two groups are on the same side is called the cis form and that in which they are on opposite sides, the trans form. The cis form of oleic acid occurs generally in nature, but the trans form is developed during hydrogenation.[1] The trans form is the more stable and has the higher melting point. The exact mechanism of the formation of iso-oleic acid has never been explained. It could be formed by hydrogenation of linoleic acid or by isomerization of cis-oleic acid; apparently its formation is due to both reactions.[1]

Little data are available on the effect of hydrogenation operating variables on the formation of iso-oleic acid. This is mainly because no reliable analytical methods were known until recently. Bailey and co-workers[12] proposed a rule: Operating conditions which favor selectivity also favor iso-oleic acid formation. They used, however, the unreliable lead salt method for analysis. They reported that the increase of temperature and increase of catalyst concentration favors the formation of iso-oleic acid, while the increase

in pressure and the improvement of agitation lowers the formation of iso-oleic acid. A reliable analytical method for the determination of iso-oleic acid has recently been reported by Swern et al[16] using the infrared absorption spectra. This method has not as yet been used to study the effect of operating variables on isomerization of a commercial oil.

From a commercial standpoint it is desirable to have a relatively rapid rate of hydrogenation so that the time the oils need to be kept in the reactors is held to a minimum. The rate of hydrogenation is defined as the drop of iodine value per unit time. The iodine value is a measurement of unsaturation and is defined as the number of grams of iodine absorbed per 100 grams of fat sample. In general, the rate of hydrogenation is increased by higher temperatures, pressures, catalyst concentration, and intimacy of contact (i.e., agitation).

Hydrogenation can take place only after hydrogen, an unsaturated fatty acid radical, and the active portion of a metallic catalyst have been brought together. In the absence of a catalyst the reaction is so slow that the catalyst should be considered not only a reaction accelerator, but for all practical purposes, an essential element of the reacting system.

Bailey[17] explained that the hydrogenation of oils involves the following sequence of operations:

1. Solution of hydrogen in the oil.
2. Adsorption of dissolved hydrogen on the catalyst.
3. Prior or later adsorption of unsaturated oil on the catalyst.
4. Reaction to form a nickel-hydrogen-oil complex.
5. Decomposition of the complex, to yield hydrogenated oil and free radical.
6. Desorption of the hydrogenated oil.

Bailey used limited experimental data to explain this mechanism. He hydrogenated several oils at conditions conducive to either low or high selectivity. He thought that the solution of hydrogen in oil and the adsorption of unsaturated oil on the catalyst were the two steps which controlled the reaction rate. He suggested that increased selectivity caused by all operating variable changes was related only to decreased concentrations of hydrogen in the reaction zone.

A recent work on the batch hydrogenation of liquid ethyl oleate to ethyl stearate has been reported by Krane.[18] He investigated the effect of pressure from 1.5 to 6.2 atmospheres, temperatures from 121 to 200°C, catalyst concentration from 0.199 to 0.356% by weight of nickel, and agitator speeds from 800 to 2400 rpm. The effect of these operating variables was studied on the various steps of the hydrogenation reaction. Krane suggested the following steps:

1. The solution of hydrogen into the liquid oil.
2. The mass transfer of the dissolved hydrogen from

the oil to the catalyst surface.

3. The chemisorption of hydrogen on the catalyst surface.

4. The mass transfer of ethyl oleate from the bulk liquid phase into the pore structure of the catalyst and to the catalyst surface.

5. The surface reaction between chemisorbed hydrogen and ethyl oleate on the catalyst surface.

The difference in the mechanisms of Bailey and Krane is that Bailey ignores the mass transfer steps, while Krane thinks there is no chemisorption of ethyl oleate on the catalyst surface. Krane found that as the operating conditions change, the relative importance of the different rate controlling steps vary. For example, at 121°C and 1.6 atmospheres the surface reaction velocity potential is the most important factor determining the rate of the reaction, whereas at 200°C and 1.6 atmospheres the mass transfer potentials of hydrogen and ethyl oleate are more important. Above 160°C the chemisorption of hydrogen is no longer an appreciable factor in determining the reaction rate. Increasing the hydrogen pressure increases the relative importance of the mass transfer of ethyl oleate as a rate determining factor. However, there is no sharp transition in the relative importance of the various rate controlling factors, and all of them must be taken into account to satisfactorily describe the course of the reaction.

Investigations of the mechanism of vapor phase hydro-

genation of ethylenic double bonds have been made with ethylene,[19] propylene,[20] and iso-octenes.[21] Catalysts used were copper-magnesia and nickel. In the hydrogenation of iso-octenes, known commercially as codimer, the nickel catalyst was used at sufficiently high mass velocity that diffusional gradients were shown to be negligible. The following ranges of operating variables were investigated: pressures from 1.0 to 3.5 atmospheres, temperatures from 200 to 325°C, and feed composition from 10 to 90 mole percent of each component. The mechanism of the reaction was explained by either a reaction between molecularly adsorbed hydrogen and adsorbed codimer where the surface reaction was controlling, or by a reaction between atomically adsorbed hydrogen and adsorbed codimer where the surface reaction was controlling. The likeliest rate controlling mechanism for the hydrogenation of propylene on a 50-50 mole % copper-magnesia between 46° and 76°C is the surface reaction between atomically adsorbed hydrogen and adsorbed propylene. A similar mechanism is proposed for the hydrogenation of ethylene.

Problem Statement

The foregoing discussions of literature survey indicate that several workers have investigated the effects of operating variables in hydrogenation of fats and oils. However, due to the lack of dependable analytical methods, these investigations were, in many cases, of an unreliable

nature. Furthermore, they were in general only qualitative. The purpose of this research was to obtain quantitative data on the effect of temperature, pressure, amount of catalyst, and agitation, on selectivity, iso-oleic acid formation, and the rate of hydrogenation, for cottonseed oil. Refined and bleached cottonseed oil was to be hydrogenated in a dead-end reactor, using electrolytic hydrogen and commercial nickel catalyst. The range of operating variables to be studied were as follows: Temperature 115 to 160°C, pressure 20 to 140 psi, catalyst 0.03 to 0.15% by weight, and agitation from 550 to 1760 rpm. The data was critically examined to find, if possible, what are the rate controlling steps on the reaction. Attempts were made to correlate the data so as to quantitatively measure selectivity and isomerization and to determine, if possible, the mechanism of each.

CHAPTER II

DESCRIPTION OF EQUIPMENT AND MATERIALS USED

Hydrogenation Apparatus

The hydrogenation runs were made in a small laboratory dead-end reactor. The assembled apparatus is shown schematically in Figure 1 and pictorially in Figure 2. Figure 3 shows the details of the reactor itself.

The reactor shell (1) was constructed from a 5 inch plain carbon steel pipe that was 12 inches long. The bottom end of the shell was closed by welding to it a 3/8 inch thick steel plate. A 400 psi steel slip-on flange was welded at the top of the shell. A 400 psi blind flange was provided to close the top of the reactor. Granite type gaskets were used to obtain a gas tight seal at the flange. The reactor was positioned and held inside a 10 3/4 inch length of 6 inch pipe (2) that was welded to the base of the apparatus. A thin layer of asbestos paper was wrapped around this length of pipe in order to serve as an insulator for the nichrome wire that was wrapped around it. Three lengths of 1.36 ohms per foot wire, each 13 feet long, were used as heaters (3) each with approximately 750 watt

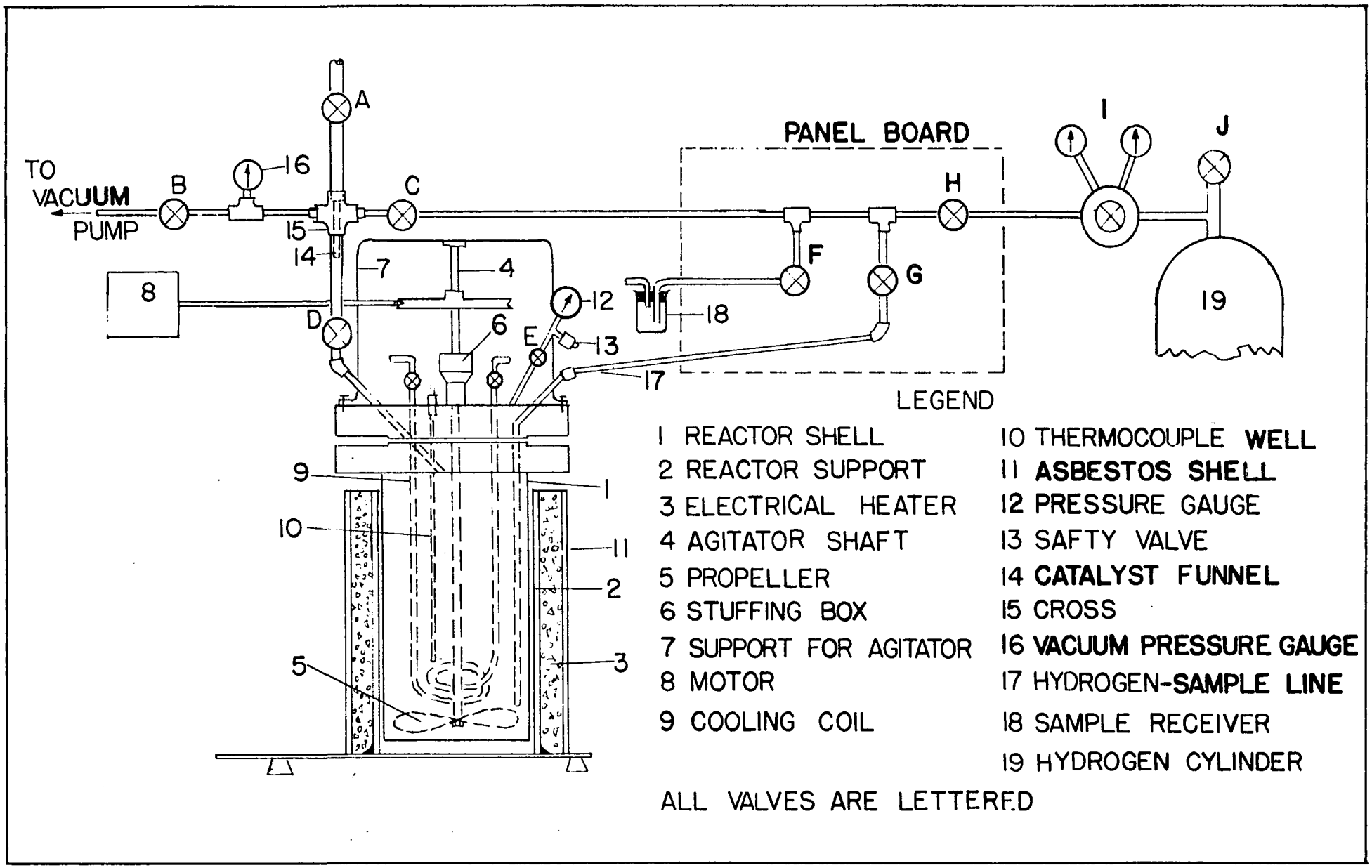


FIGURE 1 FLOWSHEET OF HYDROGENATION APPARATUS

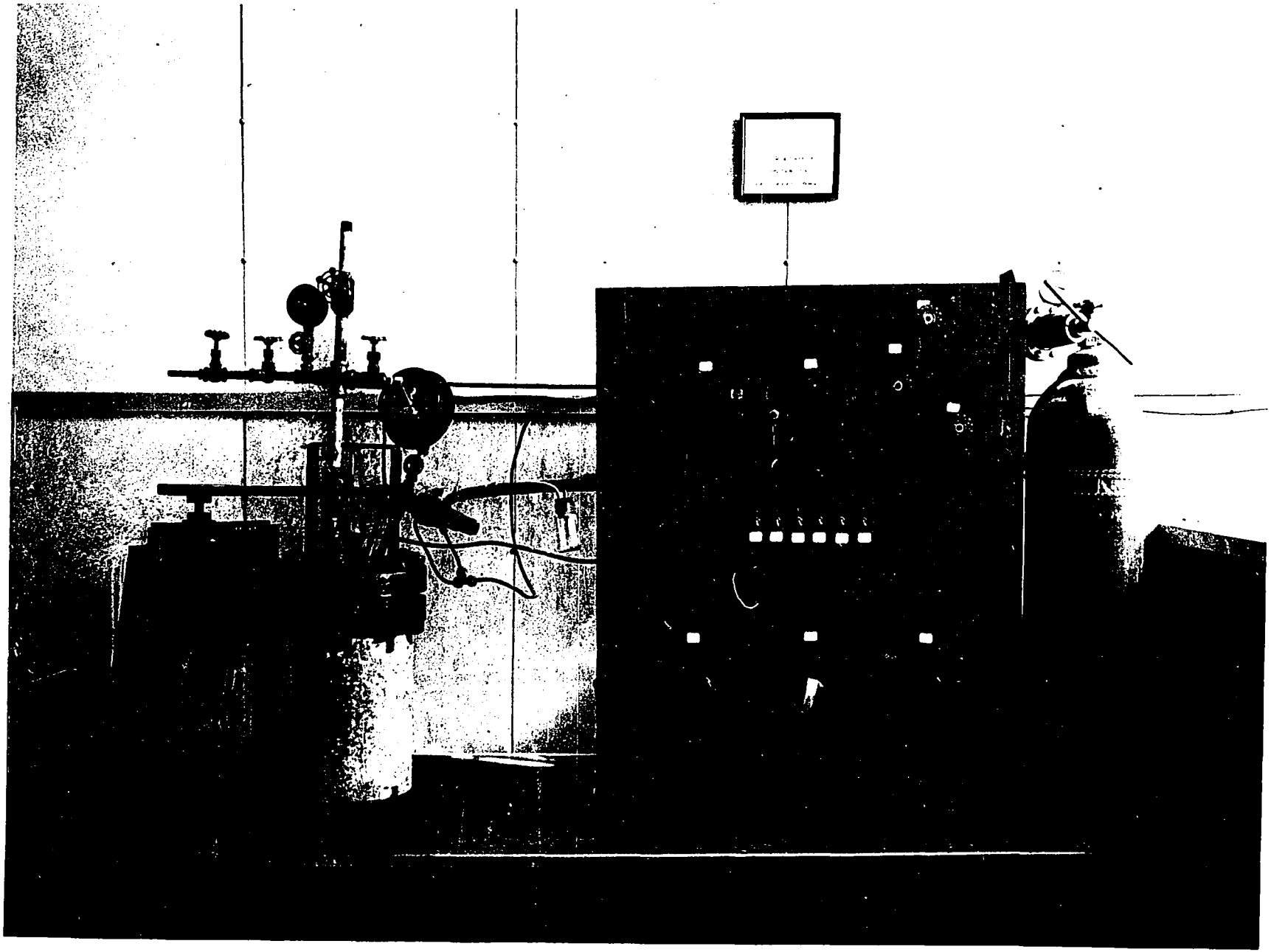


Figure 2. Illustration of Hydrogenation Apparatus

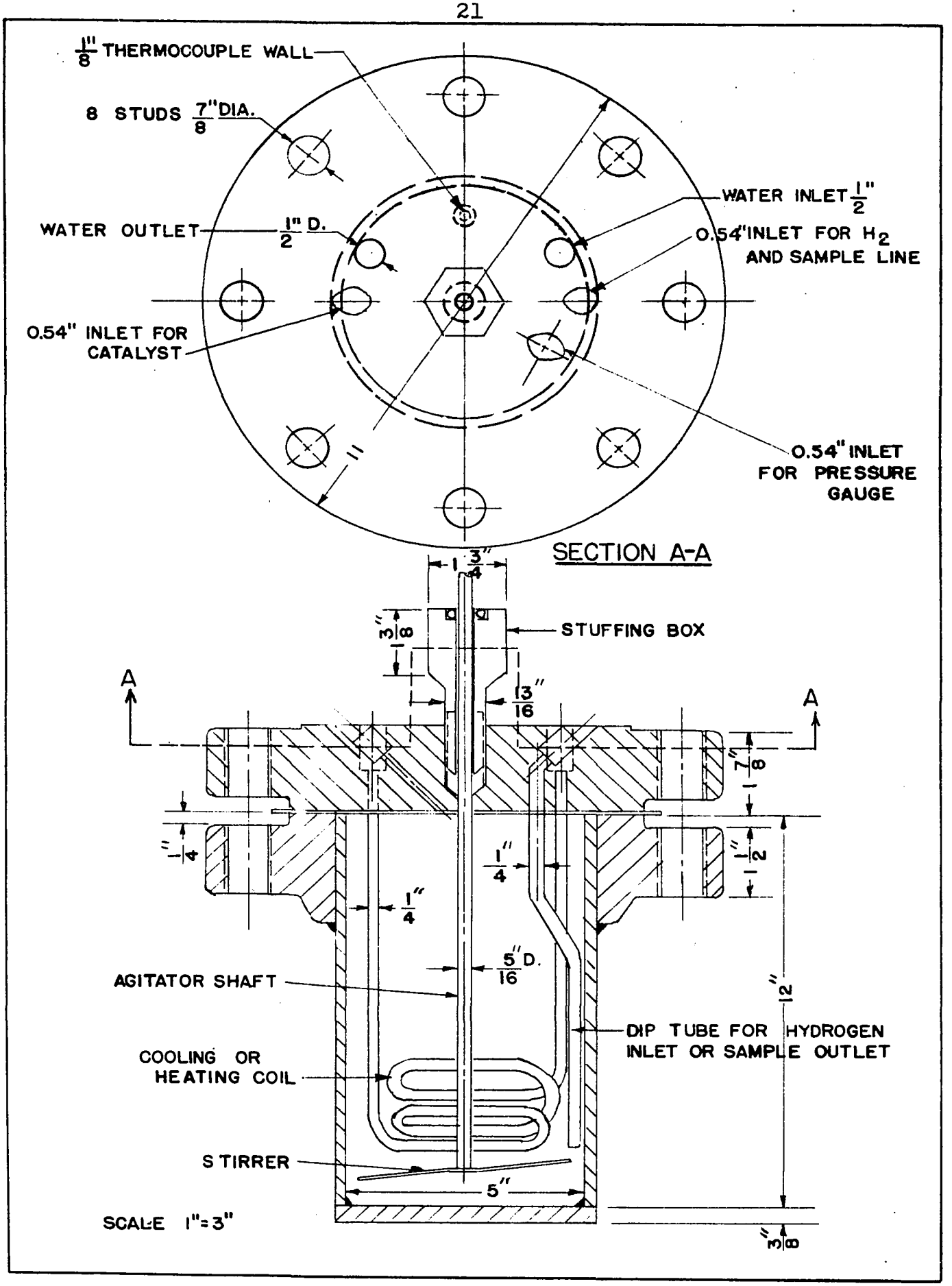


FIGURE 3 REACTOR DETAIL

capacity. A coaxial transformer was provided to regulate the voltage to each heater. Asbestos paper was wrapped around the heaters, and a heavy walled (3/8 inch thick) asbestos shell (11) was positioned around the pipe.

The reactor was equipped with an agitator shaft (4), made of 5/16 inch diameter plain carbon steel rod which passed through the middle of the blind flange. A propeller (5) was positioned on the rod approximately one inch from the bottom of the reactor. The propeller was made of a circular (4 inch diameter) stainless steel plate, 1/4 inch thick. Four notches were cut in this plate 90° apart, and each section was inclined at a 15° angle. The propeller was fastened to the rod by a screw embedded in its bottom tip. A stuffing box (6) was provided to prevent gas leakage around the shaft. The stuffing box shell was made of brass. The top part of it was hexagonal in shape, and the bottom part screwed inside the blind flange to a depth of around 1 inch. Graphited asbestos was used as the packing. A small ball bearing at the top of the stuffing box absorbed most of the lateral stress of the agitator shaft. In order to minimize bending of the agitator shaft, a support (7) was provided. The support was made of a steel bar 1/4 inch thick and 1 inch wide and was fastened to the reactor by means of two set screws in the blind flange. A ball bearing was installed on the support to position the top of the agitator shaft. A pulley was mounted on the agitator shaft

about 5 inches above the reactor. Power from a 1/4 hp constant speed (1760 to 1780 rpm) electric motor (8) was transmitted to the pulley by a V-belt. The motor shaft was provided with a variable diameter pulley, which allowed the speed of the agitator to be varied.

Two openings were provided in the blind flange for the exit and entrance of a cooling coil (9) made of 1/4 inch low carbon steel tubing. The coil consisted of two turns, each approximately 4 inches in diameter, and it was positioned about 1/2 inch above the agitator propeller. The cooling coil was connected so that either steam or water could flow through it. A third opening in the blind flange was provided for a thermocouple well (10) which was made of 3/8 inch low carbon steel tubing welded shut at the lower end. The end of the tubing was immersed in the reactor to within about 2 inches above the bottom. An iron-constantan thermcouple and a Leeds-Northrup potentiometer were used to measure the temperature to within 0.5°C. A fourth opening in the reactor flange was provided for a sample draw-out or hydrogen inlet line (17). It was constructed of steel and was immersed within about 1 inch from the bottom of the reactor. A fifth opening in the reactor flange was provided for a calibrated pressure gauge (12). The gauges used varied in range and were as follows:

(a) 0 to 40 psig

(b) 0 to 160 psig

(c) 0 to 300 psig

The pressure being studied usually appeared close to the middle of the gauge dial. A safety valve (13) was connected to the reactor through the same line that supported the pressure gauge. This safety valve was of the spring type and was set to open at a pressure of 300 psig. Pressure tests indicated it operated satisfactorily at such a pressure.

A sixth opening in the reactor flange was provided for catalyst introduction. The catalyst reservoir was a 1/2 x 4 inch nipple which was connected at the top of a 1/2 inch globe valve (A). The lower side of the valve opened through a nipple to a funnel (14) positioned inside a 1/2 inch cross (15). The lower side of the cross was connected to a 1/2 x 6 inch nipple which screwed into the top of a 1/2 inch globe valve (D). The bottom of this valve was connected by a 1/4 x 6 inch nipple to the sixth opening on the top flange. The cross (15) was connected on one side to a pressure-vacuum gauge (16), a valve (B), and a Hyvac vacuum pump. The other side of the cross (15) was connected to a valve (C) which in turn was connected through valve (H) to the hydrogen regulator valve (I) and the hydrogen cylinder (19). Valve (F) opened to the sample receiver (18). Valve (G) connected the hydrogen supply coming through valve (H) to line (17), the latter was connected to the fourth opening in the reactor top by a 1/4 inch pipe arrangement.

In Figure 2, valves for steam and water, bystand valves, switches, and co-axial transformers appear on the panel board. These are not shown in Figure 1.

Analytical Equipment and Supplies

Iodine Values

Iodine values were determined using approximately 0.2 N Wijs solution obtained from Fisher Scientific Company. Standard 500 ml iodine flasks were used for these determinations.

Ultraviolet Analysis

A model DU Beckman Ser. 2925 Spectrophotometer manufactured by the National Technical Laboratory in South Pasadena, California, was used for the quantitative determination of linoleic acid. Quartz cells, 0.997 cm thick, were used to hold the samples. Absolute (100%) ethyl alcohol was used as a solvent for the fat samples.

Infrared Analysis

A Perkin-Elmer Infrared Spectrometer, Model 12C, Serial 431, was used for the quantitative determination of trans iso-oleic acid. A cell with sodium chloride crystal windows was used. The cell thickness was 0.1 cm. The solvent used for the samples was reagent grade carbon disulphide.

Materials Used

The cottonseed oil used for the hydrogenation runs was obtained from "Mrs. Tuckers' Products" in Sherman, Texas. The oil was refined and bleached and had an iodine value of 103.5. It consisted of 47% linoleic acid, 27.45% oleic acid, and 25.55% stearic acid. The oil was stored in a cold room at 49° until just before use. The hydrogen gas used was of the electrolytic type and was 99.5% pure. Hydrogen cylinders were purchased from the National Cylinder Gas Company. The catalyst used was Rufert nickel catalyst. It was obtained from the Harshaw Chemical Company and was reported by the vendor to contain 24.45% nickel.

CHAPTER III

EXPERIMENTAL TECHNIQUES

Operation of the Hydrogenation Equipment

Before a hydrogenation run was started, the top of the reactor was removed, and hot (200°F) refined cottonseed oil was added to the reactor to rinse out all old catalyst and oil. This oil was then drained by tipping the reactor, and the residual oil was lightly wiped from the reactor with a clean rag.

The oil to be hydrogenated was weighed by means of a balance, accurate to within a gram. A total of 1400 grams of refined cottonseed oil were added to the reactor. This quantity was sufficient to fill the reactor about two-thirds full. The top of the reactor was positioned, bolted, and then tightened. An asbestos gasket coated with a thin film of refined cottonseed oil was used on the reactor to prevent leakage at high pressures. The reactor was positioned inside the reactor support (2). The pulley on the agitator was connected by means of a V-belt to the motor (8) driving the agitator. The overhead support (7) was installed. The reactor was connected to the hydrogen supply line (17), and

to the valve (F) through valve (C). The reactor was also connected to the cooling water line and to the vacuum source of the system. The thermocouple was inserted in its well.

The reactor was evacuated, and the cottonseed oil was deaerated by applying a vacuum to the system. In order to do this, valves (J), (G), (F), (E), and (A) were closed, and all other valves were opened. The vacuum pump was then operated, and the pressure inside the reactor dropped to approximately 1" Hg absolute, as indicated by the vacuum-pressure gauge (16). This pressure was maintained for a period of approximately five minutes to insure deaeration of the oil. Valves (D) and (C) were closed, the vacuum pump was turned off, and valve (J) was opened. The pressure regulating valve (I) was set to regulate the hydrogen pressure about 10 to 20 psig. below that desired for the run. Valves (H) and (G) were opened, and the hydrogen flow to the reactor was started through line 17. Immediately valve (E) on the pressure gauge was opened to indicate the pressure inside the reactor. After the hydrogen in the reactor reached the desired pressure, valves (G) and (H) were closed. The agitator (5) was now started, and the heaters (3) were turned on. The system was inspected for leaks, using a soap solution. If there were any leaks, they were immediately repaired. Readings of the temperature inside the reactor were observed and recorded approximately every five minutes. It was noticed that the hydrogen pressure

increased during the heating period. When it went above the planned operating pressure, valves (D) and then (A) were opened, and some hydrogen was vented in order to maintain a pressure inside the reactor always 5 psi below the planned operating pressure.

When the temperature in the reactor reached a point about 10°C below the planned operating temperature, an amount of catalyst, weighed to within ± 0.0001 grams, was dissolved in 50 grams of hot refined cottonseed oil contained in glass beaker. The temperature of the oil was usually about 10°C higher than the operating temperature desired for the run. After the catalyst was dissolved it was poured from the beaker into the nipple above valve (A). The catalyst reservoir above valve (D) was now evacuated by means of the vacuum pump. Valve (B) was then closed, valve (H) opened, and the regulator (I) on the hydrogen cylinder set to discharge hydrogen at the planned operating pressure as indicated by gauge (16). Valve (C) was then closed, valve (B) was opened, and the reservoir above valve (D) was evacuated. Valve (B) was now closed, and valve (A) was opened. The catalyst in the oil solution drained through funnel (14) in the reservoir above valve (D). Valve (A) was closed, and valve (B) was opened. The space now above the catalyst solution above valve (D) was evacuated for a few seconds, valve (B) was closed, and valve (C) opened. This caused a pressure equivalent to the operating pressure to be exerted

on the surface of the catalyst solution in the reservoir above valve (D). This pressure was slightly higher than the pressure inside the reactor. Valve (D) was then opened, and the catalyst was forced inside the reactor. This was considered to be the start of the hydrogenation run, and the time, temperature, and pressure were measured and recorded. The method explained above to introduce the catalyst insures that only catalyst, oil, and hydrogen are inside the reactor, and that air is eliminated during the reaction, since the presence of air is hazardous and deactivates the catalyst.

In order to insure that all the catalyst was in the reactor, the beaker that had contained the catalyst was rinsed with 50 more grams of hot refined cottonseed oil. This oil was then added to the reactor in the same manner the main batch of the catalyst had been. As soon as the process of adding all the catalyst was completed, valves (D) and (C) were closed, and valve (G) was opened. The pressure inside the reactor had dropped slightly after the catalyst was added, but the pressure regulating valve (I) now maintained a constant hydrogen pressure during the run.

Since hydrogenation is an exothermic reaction, an increase in temperature was observed when the catalyst was added. Temperature increases as high as $5^{o}C$ were noted. In general, after the addition of the catalyst the heaters were turned off, and steam was occasionally throttled inside the reactor cooling coil to bring the temperature down to the

operating conditions. Using this method, the temperature during the run was manually controlled to within ± 2°C. The pressure was kept constant to probably less than ± 1 psi by the pressure regulating valve (I) on the hydrogen cylinder. The speed of the agitator remained constant to within 20 rpm as measured at frequent intervals by a tachometer. The temperatures and pressures during the run were recorded every three to five minutes, depending upon the length of the run and the expected rate of hydrogenation.

Six to seven samples were taken during the run, about 10 to 15 iodine value units apart. The time intervals between samples varied from 3 to 6 minutes at high temperatures such as 160°C or high pressures such as 140 psig, or from 30 to 45 minutes at mild operating conditions such as a temperature of 115°C or a pressure of 20 psig. Fifteen seconds before the time to obtain a sample, the line leading to the sample bottle (18) was flushed with hydrogen by opening valve (F), then closing it. Valve (H) was closed, and valves (F) and then (C) were opened. The first 10 to 15 grams of the sample drawn out were discarded. The next 20 to 40 grams were collected in a clean sample bottle. A slight drop of pressure inside the reactor was noticed while the sample was being drawn out. Valves (F) and (G) were then closed, and valve (H) was opened. Then valve (G) was opened, and the pressure inside the reactor returned to operating pressure. Valve (F) was now opened carefully, and

the hydrogen gas flushed out any oil entrained in the line leading to the sample bottle.

After a sample was collected, the catalyst was separated from the hydrogenated oil by filtration. Two sheets of No. 2 filter paper were used for each sample. After the sample was poured on the filter paper in the funnel, the funnel was transferred to an oven maintained at a temperature slightly lower than 140°F. The heat of the oven kept the sample from solidifying on the filter paper. Usually after about 20 minutes in the oven sufficient clear oil was obtained for analytical purposes.

When all the desired oil samples were collected, the heat was turned off the reactor, and the agitation was stopped. The hydrogen pressure on the reactor was vented through valves (D) and (A) to the atmosphere. The reactor was opened, and hot refined cottonseed oil was poured into the reservoir above valve (A). The oil was then collected from the opening leading to the reactor. The color of the oil collected was always clear, indicating that all the catalyst was removed from inside the catalyst chamber and the lines connecting it to the reactor proper. The reactor was then assembled, and the hydrogenated oil left in until a future run. This was done to prevent poisoning of the reactor by air or any contaminants.

Analytical Procedures

The refined cottonseed oil and the hydrogenation samples were analyzed for unsaturation by an iodine value determination as recommended by the American Oil Chemists' Society.[22] These samples were analyzed for linoleic acid, using the ultra-violet absorption spectra as explained by Brice et al.[7] The isomerization period of the unconjugated dienes was altered in this analysis from 30 to 45 minutes as suggested by O'Connor et al.[23] The triglyceride samples were also analyzed for iso-oleic acid, using the infra-red absorption spectra, as explained by Swern et al.[15]

CHAPTER IV

RESULTS

Thirteen hydrogenation runs were made over the following range of operating conditions:

(1) Temperature, 115 to 160°C

(2) Pressure, 20 to 140 psig

(3) Catalyst concentration, 0.03 to 0.15% nickel by weight

(4) Agitation from 550 to 1760 rpm.

When one variable was being studied, all other variables were held constant. The experimental results of these runs are shown in Tables III to XV in Appendix A. A run representing average operating conditions (i.e., 130°C, 60 psig, 0.07% nickel catalyst, and 1175 rpm) was repeated twice (Runs 1 and 11) during the project. The results of these check runs appear in Tables III and XIII, and indicate good reproducibility.

Plots of the logarithm of the iodine value (I.V.) versus time were made for all experimental runs as shown in Figures 4 to 7. The plot for the average run (130°C, 60 psig, 0.07% nickel catalyst, and 1175 rpm), as plotted here, was the average of Runs 1 and 11. In Figures 4 to 7, the

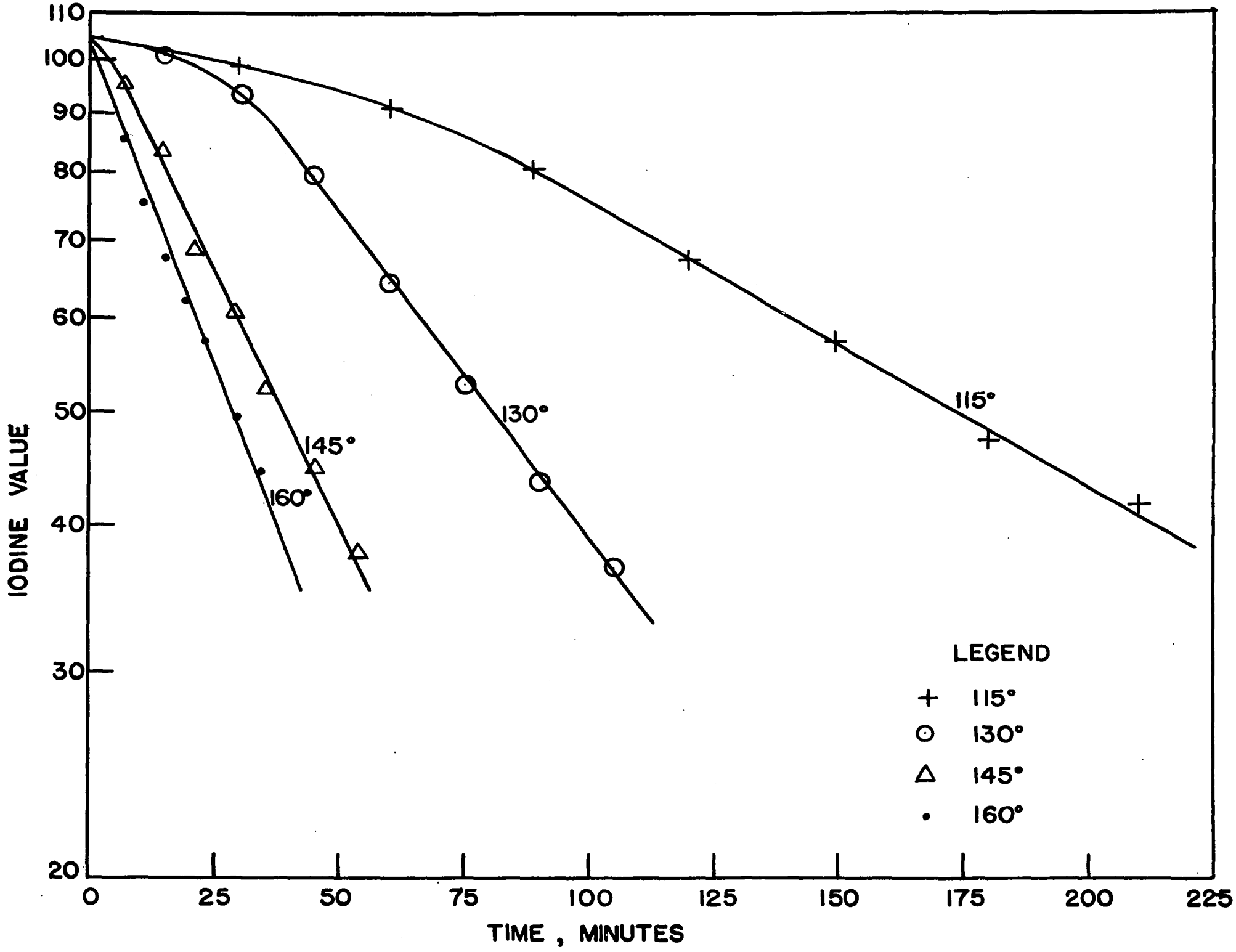


FIGURE 4 EFFECT OF TEMPERATURE ON HYDROGENATION RATE

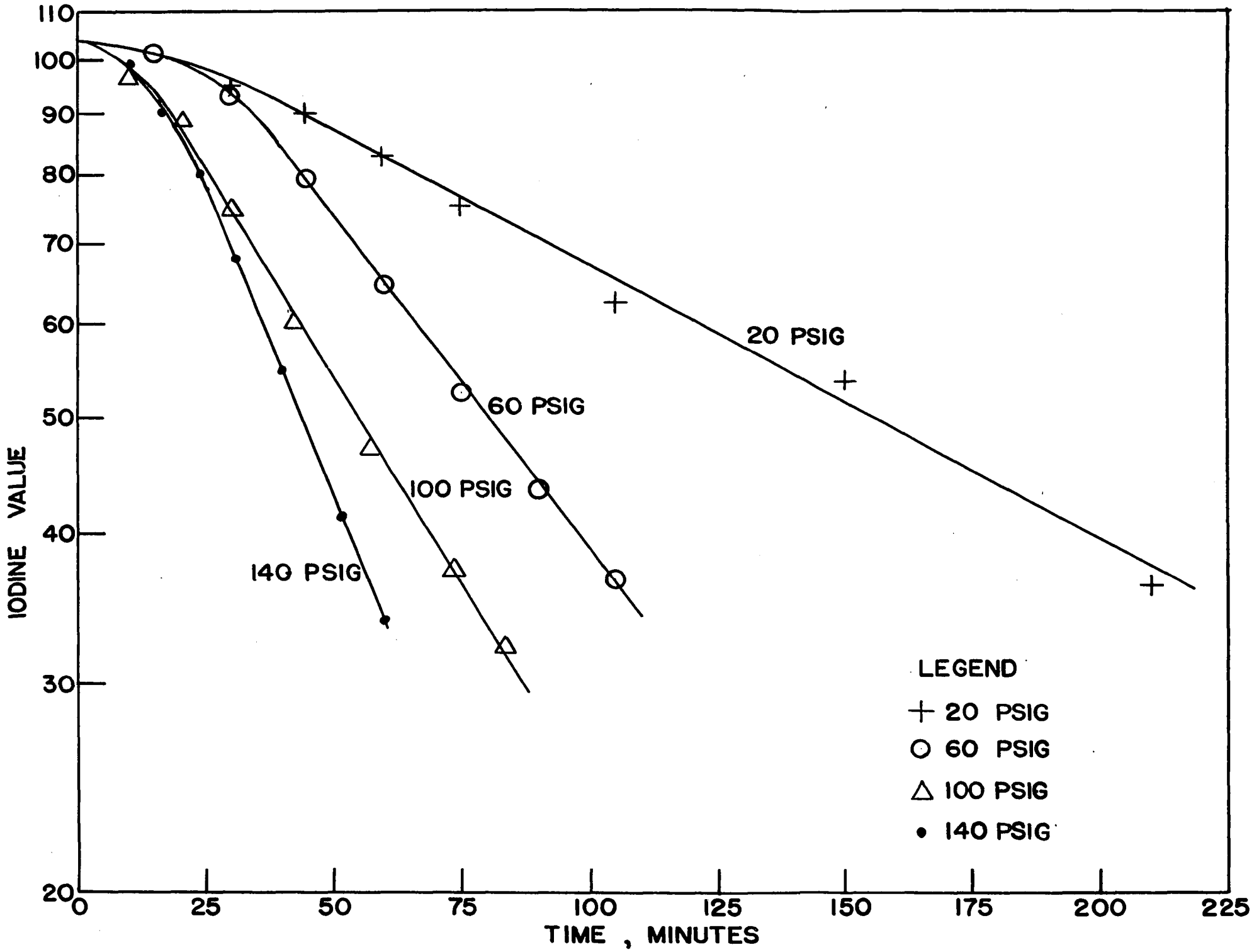


FIGURE 5 EFFECT OF PRESSURE ON HYDROGENATION RATE

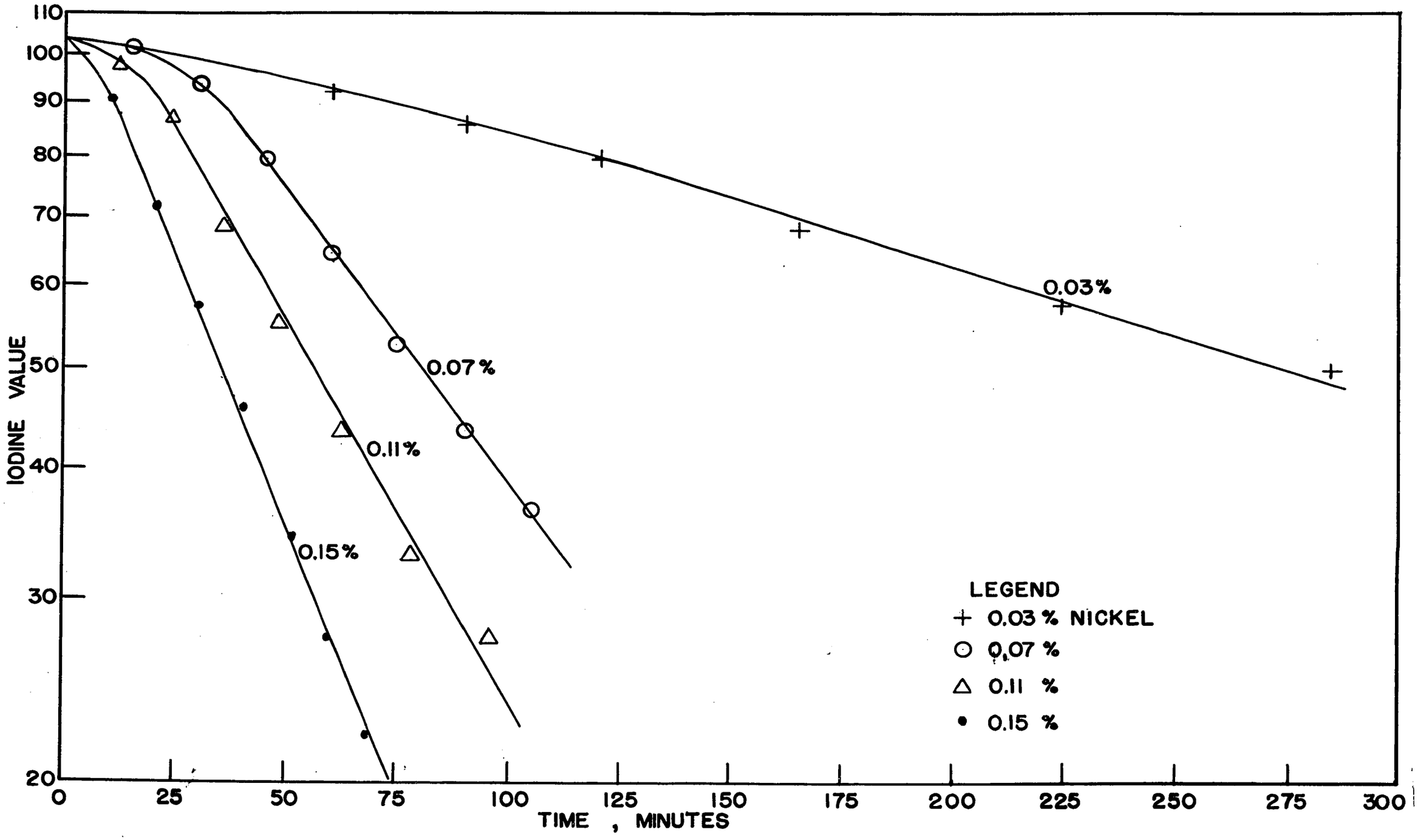


FIGURE 6 EFFECT OF CATALYST CONCENTRATION ON HYDROGENATION RATE

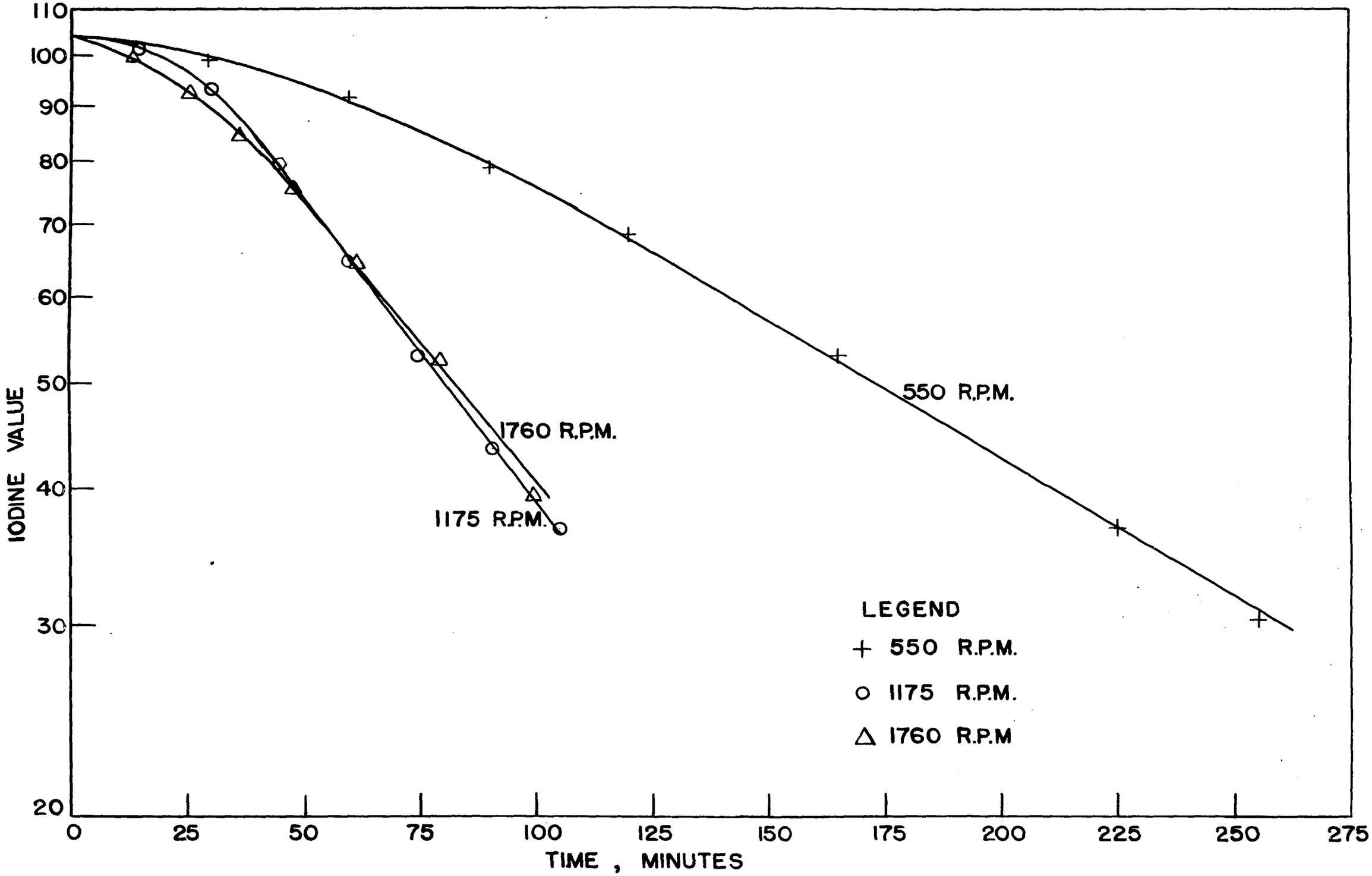


FIGURE 7 EFFECT OF AGITATION ON HYDROGENATION RATE

data below 80 I.V. are represented within experimental accuracy by straight lines. The negative slopes of these straight lines are the pseudo first order reaction rate constants, k', in the following equation:

$$r = k' \quad (I.V.) \qquad (IV - 1)$$

where

r = I.V. drop per minute

Experimental values of k' for each run are shown in Table I.

TABLE I

EXPERIMENTAL AND CALCULATED VALUES OF REACTION RATE CONSTANTS FOR HYDROGENATION RUNS

Run No.	Descriptive Parameter	k' (experimental)	k' (calculated)	% deviation
1, 11	Average	0.0128	0.0116	- 9.4
2	145°	0.0184	0.0180	- 1.7
3	160°	0.0253	0.0241	- 0.3
4	115°	0.00557	0.00516	- 7.9
5	0.03% Ni	0.00295	0.00496	+68.0
6	0.11% Ni	0.0169	0.0182	+ 7.4
7	0.15% Ni	0.0239	0.0248	+ 3.8
8	20 psig	0.00559	0.00539	- 3.6
9	100 psig	0.0163	0.0178	+ 8.9
10	140 psig	0.0238	0.0240	+ 0.8
12	1760 rpm	0.00653	0.0116	+79.5
13	550 rpm	0.0119	0.0116	- 2.5

The experimental data for the average runs 1 and 11 were plotted as weight percent linoleic and iso-oleic acid versus I.V., as shown in Figure 8. This plot indicates good reproducibility of these data. Similar experimental data for the other runs were plotted as shown in Figures 9 to 12. The data are in each case represented by relatively smooth curves. The percentage total oleic acid was then calculated from the following relationship.(1)

$$\text{Iodine Value} = \frac{86.01(\%\ \text{Oleic}) + 173.2(\%\ \text{Linoleic}) + 261.61(\%\ \text{Linolenic})}{100} \qquad \text{(IV - 2)}$$

The stearic acid was calculated by difference so that the acid totals are 100 percent. The percentages of these two acids were then plotted versus iodine value as shown in Figures 13 to 16 and the results are tabulated in Tables XVI to XXVII in Appendix B.

The Effect of Temperature

The values of k' (i.e., pseudo first order reaction rate constant) for runs 1 and 11, 2, 3, and 4 were plotted as a function of temperature as shown in Figure 17. The points follow essentially a straight line which increases in value with temperature. This indicates the overall rate of hydrogenation (defined as I.V. drop per minute) is essentially linear with temperature when all other variables are constant. An extrapolation of this straight line shows that

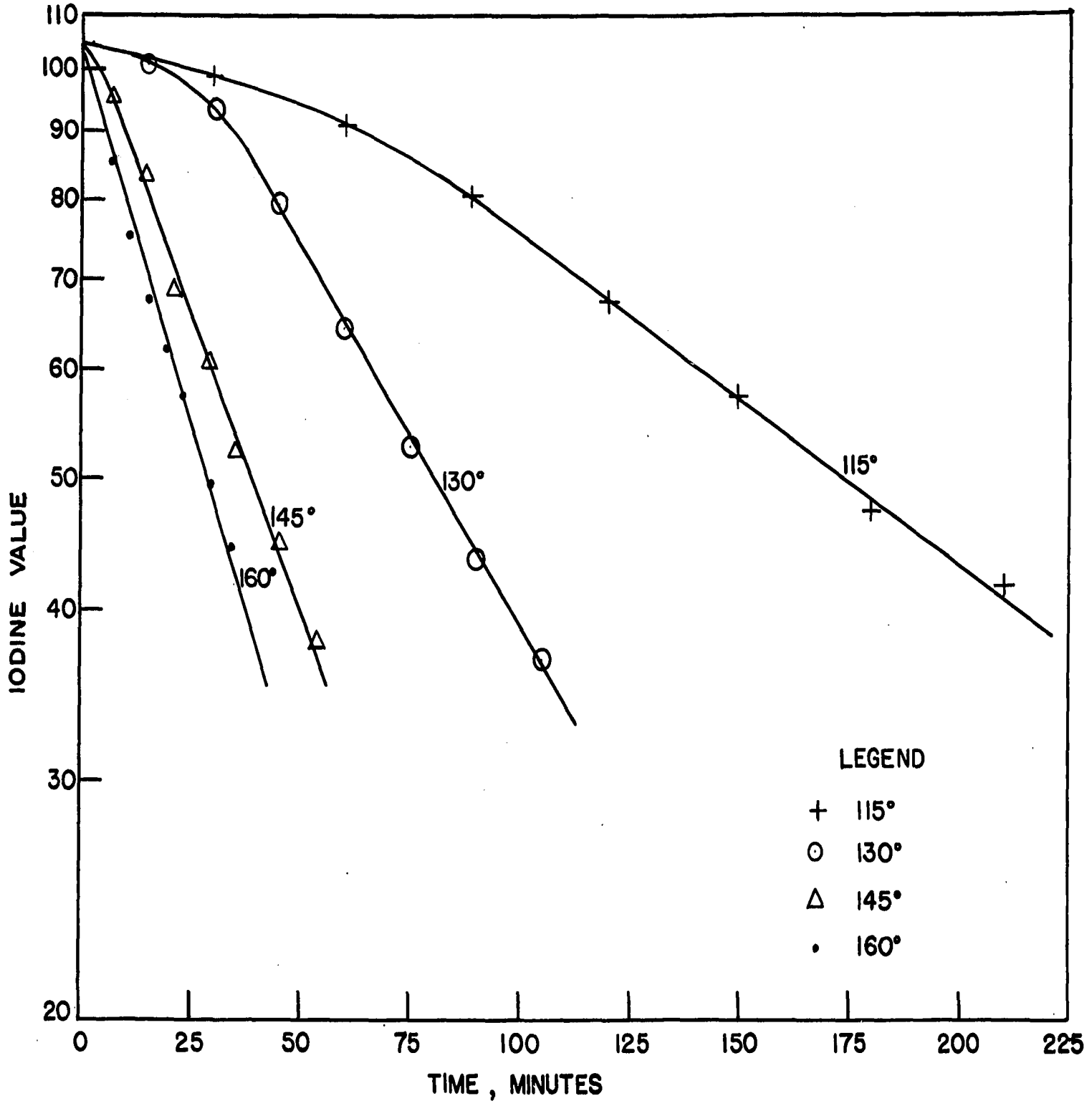


FIGURE 4 EFFECT OF TEMPERATURE ON HYDROGENATION RATE

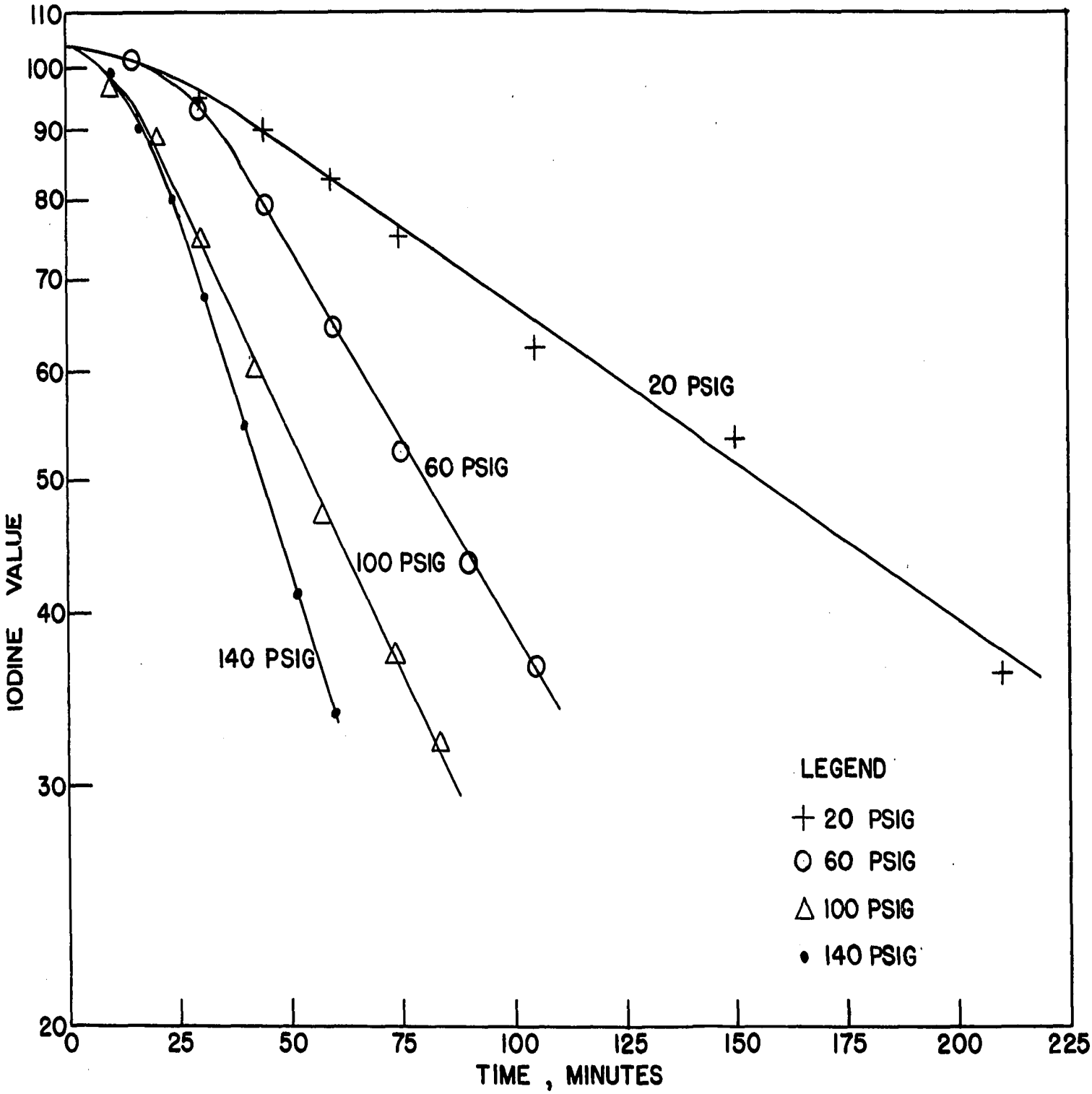


FIGURE 5 EFFECT OF PRESSURE ON HYDROGENATION RATE

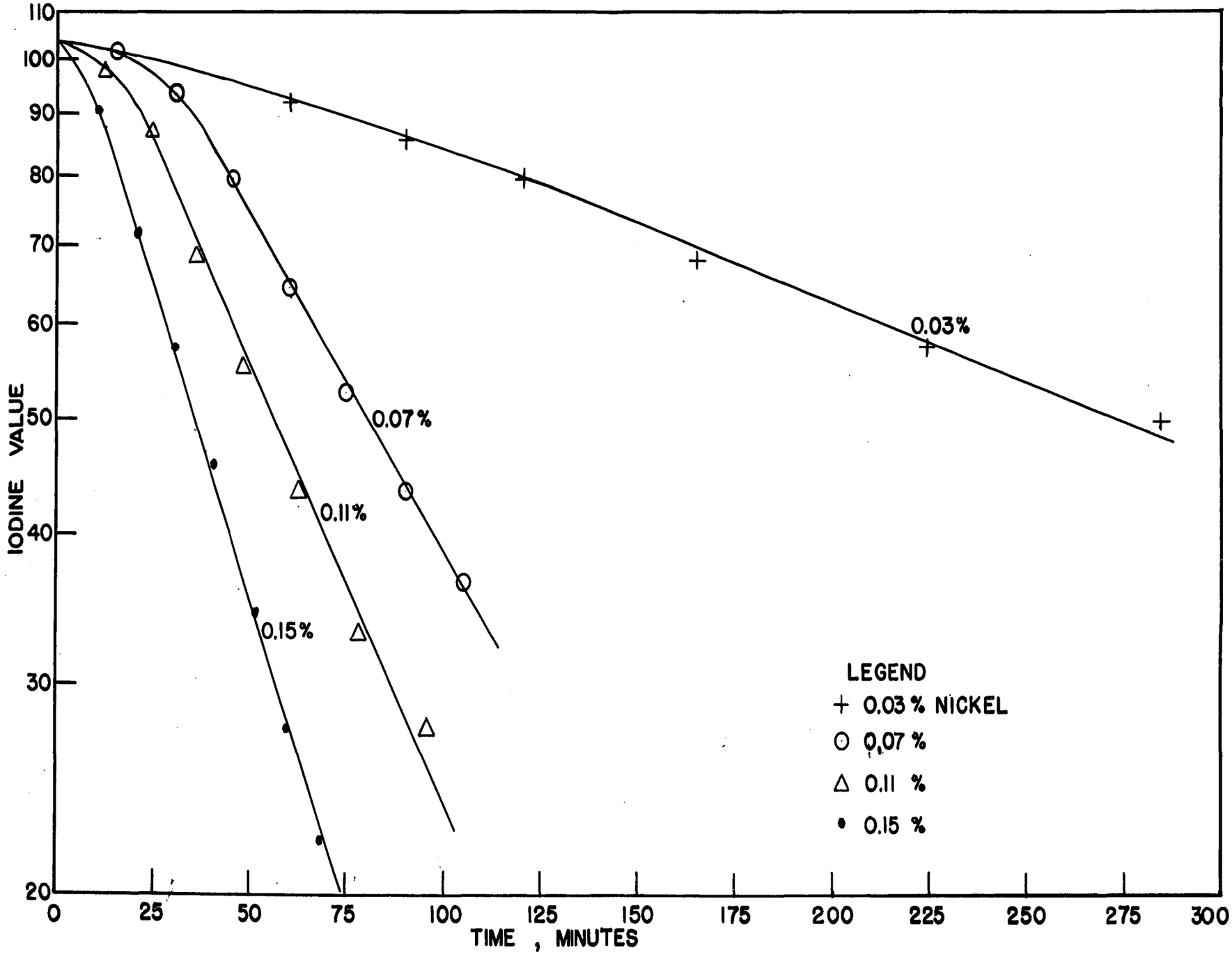


FIGURE 6 EFFECT OF CATALYST CONCENTRATION ON HYDROGENATION RATE

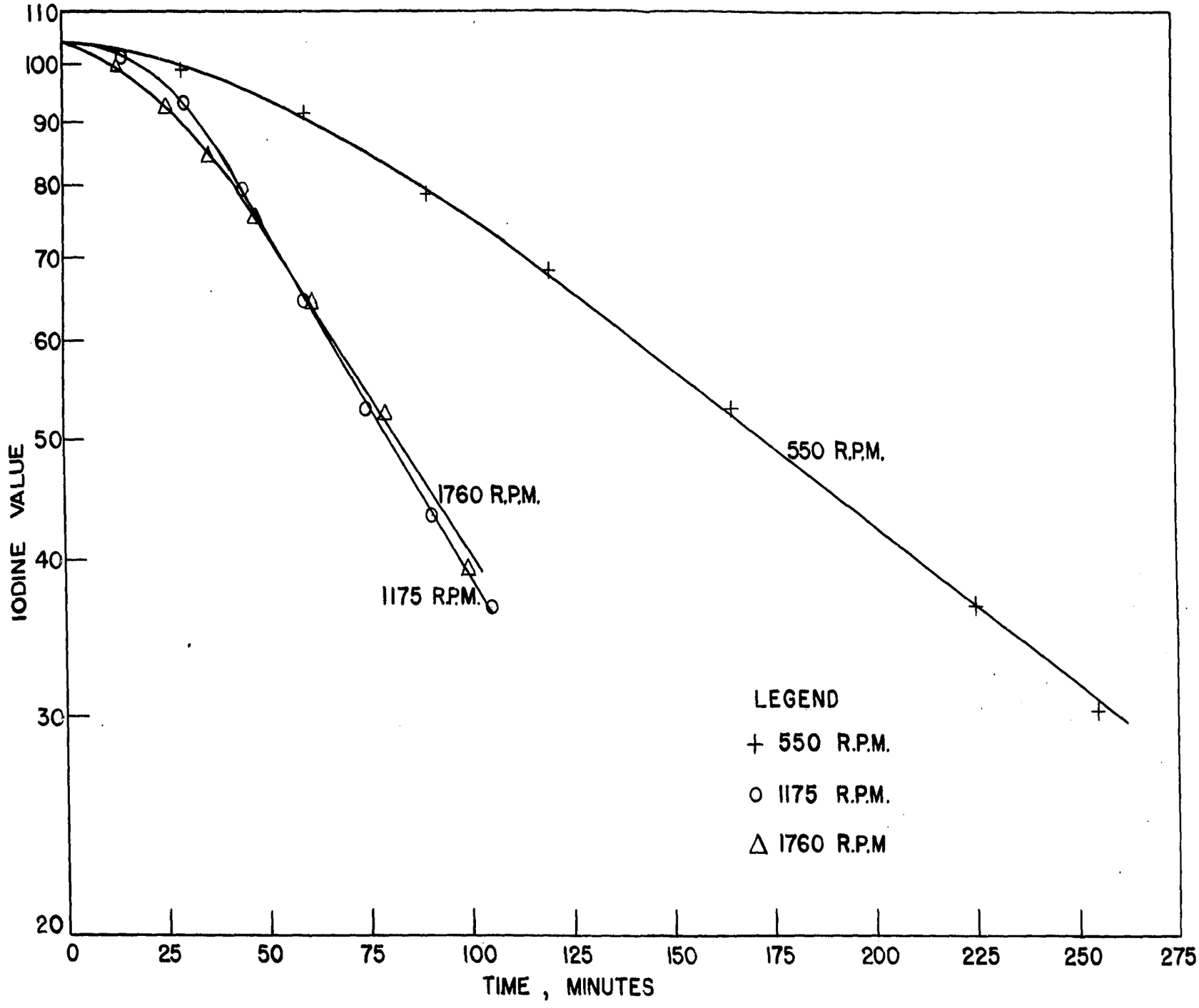


FIGURE 7 EFFECT OF AGITATION ON HYDROGENATION RATE

data below 80 I.V. are represented within experimental accuracy by straight lines. The negative slopes of these straight lines are the pseudo first order reaction rate constants, k', in the following equation:

$$r = k' \quad (I.V.) \qquad (IV - 1)$$

where

r = I.V. drop per minute

Experimental values of k' for each run are shown in Table I.

TABLE I

EXPERIMENTAL AND CALCULATED VALUES OF REACTION RATE CONSTANTS FOR HYDROGENATION RUNS

Run No.	Descriptive Parameter	k' (experimental)	k' (calculated)	% deviation
1, 11	Average	0.0128	0.0116	- 9.4
2	145°	0.0184	0.0180	- 1.7
3	160°	0.0253	0.0241	- 0.3
4	115°	0.00557	0.00516	- 7.9
5	0.03% Ni	0.00295	0.00496	+68.0
6	0.11% Ni	0.0169	0.0182	+ 7.4
7	0.15% Ni	0.0239	0.0248	+ 3.8
8	20 psig	0.00559	0.00539	- 3.6
9	100 psig	0.0163	0.0178	+ 8.9
10	140 psig	0.0238	0.0240	+ 0.8
12	1760 rpm	0.00653	0.0116	+79.5
13	550 rpm	0.0119	0.0116	- 2.5

The experimental data for the average runs 1 and 11 were plotted as weight percent linoleic and iso-oleic acid versus I.V., as shown in Figure 8. This plot indicates good reproducibility of these data. Similar experimental data for the other runs were plotted as shown in Figures 9 to 12. The data are in each case represented by relatively smooth curves. The percentage total oleic acid was then calculated from the following relationship.(1)

$$\text{Iodine Value} = \frac{86.01(\%\ \text{Oleic}) + 173.2(\%\ \text{Linoleic}) + 261.61(\%\ \text{Linolenic})}{100} \qquad \text{(IV - 2)}$$

The stearic acid was calculated by difference so that the acid totals are 100 percent. The percentages of these two acids were then plotted versus iodine value as shown in Figures 13 to 16 and the results are tabulated in Tables XVI to XXVII in Appendix B.

The Effect of Temperature

The values of k' (i.e., pseudo first order reaction rate constant) for runs 1 and 11, 2, 3, and 4 were plotted as a function of temperature as shown in Figure 17. The points follow essentially a straight line which increases in value with temperature. This indicates the overall rate of hydrogenation (defined as I.V. drop per minute) is essentially linear with temperature when all other variables are constant. An extrapolation of this straight line shows that

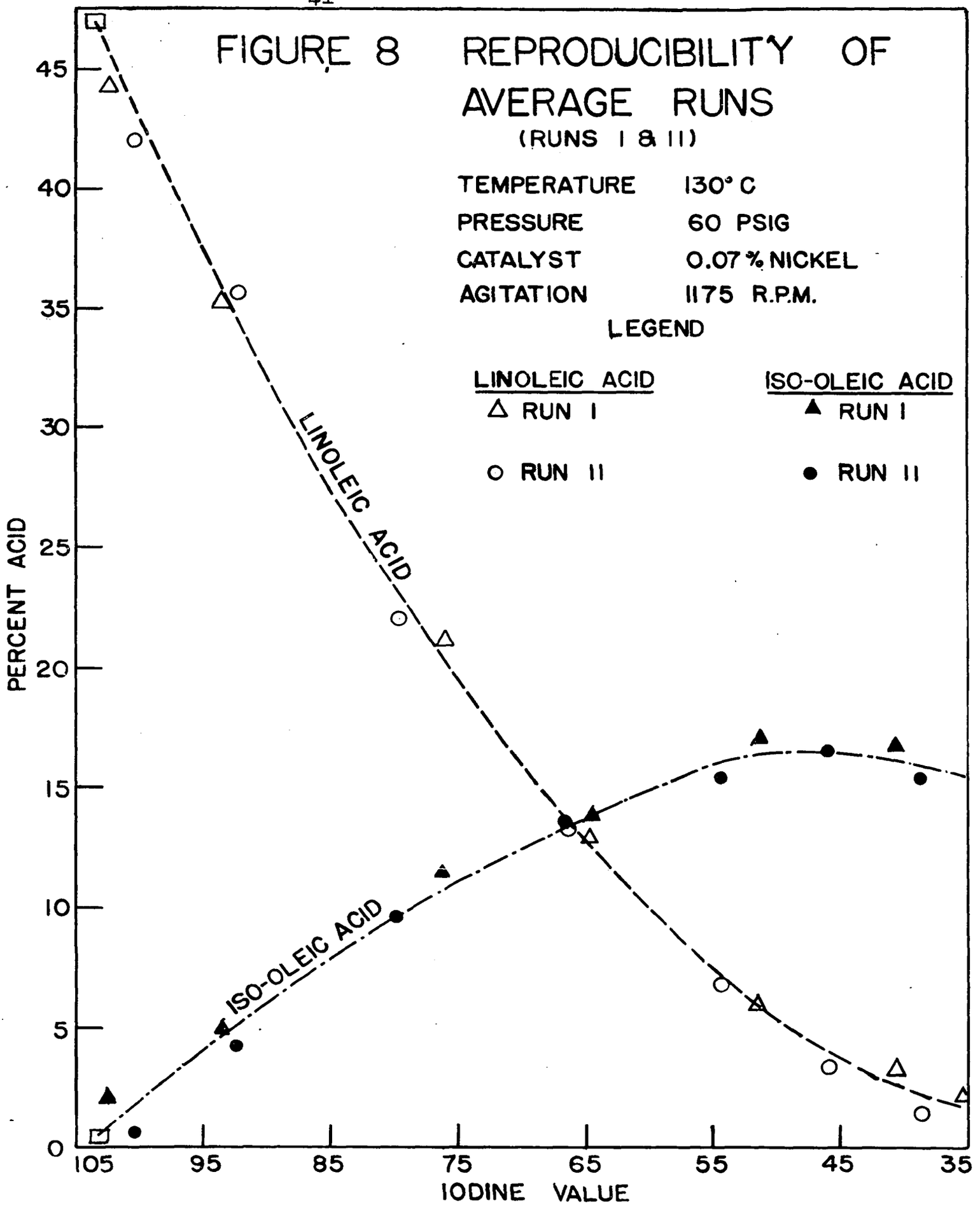


FIGURE 8 REPRODUCIBILITY OF AVERAGE RUNS
(RUNS I & II)
TEMPERATURE 130° C
PRESSURE 60 PSIG
CATALYST 0.07 % NICKEL
AGITATION 1175 R.P.M.
LEGEND
LINOLEIC ACID
△ RUN I
○ RUN II
ISO-OLEIC ACID
▲ RUN I
● RUN II
LINOLEIC ACID
ISO-OLEIC ACID
PERCENT ACID
0
5
10
15
20
25
30
35
40
45
105
95
85
75
65
55
45
35
IODINE VALUE

FIGURE 9 EFFECT OF TEMP. ON SELECTIVITY AND ISOMERIZATION

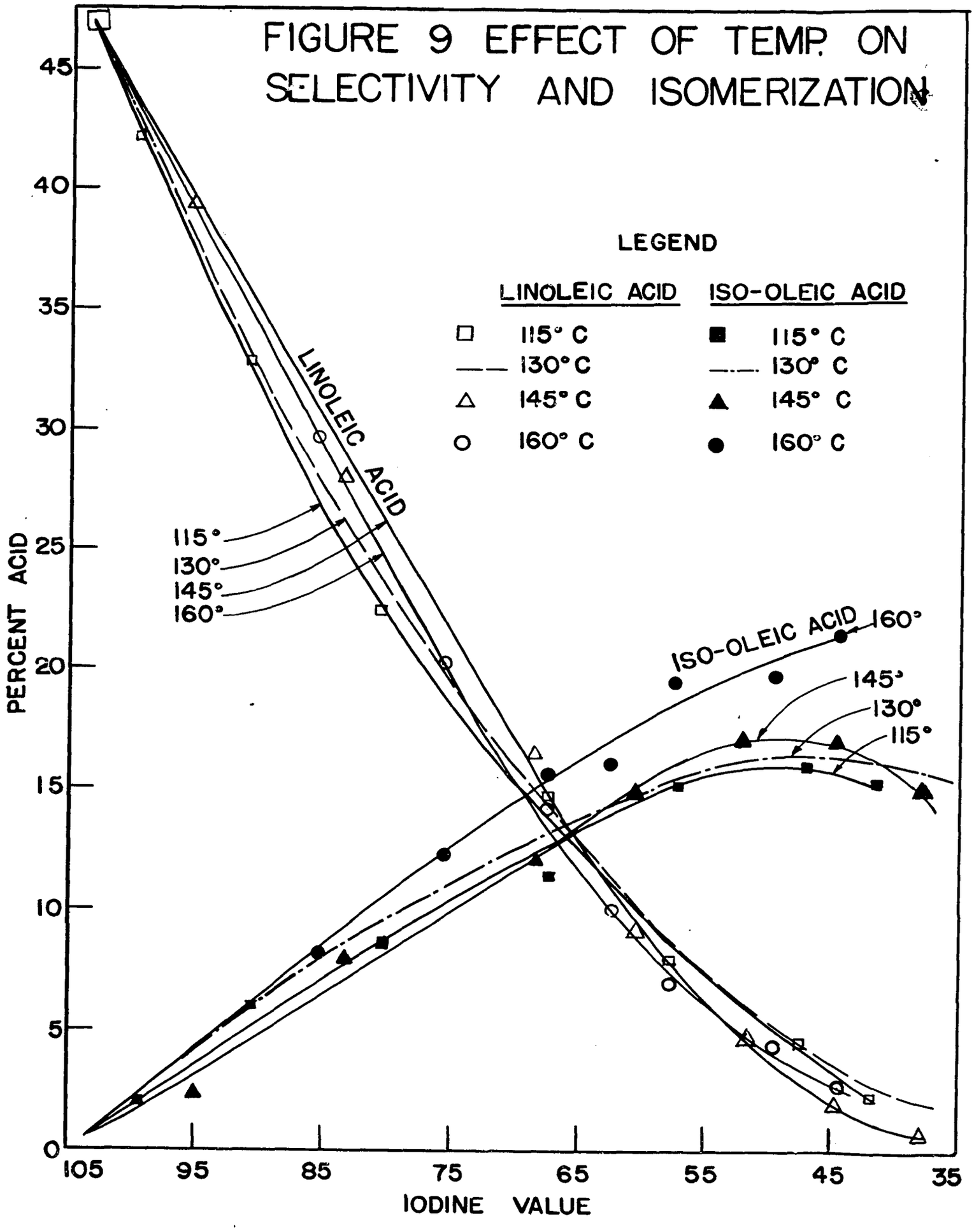


FIGURE 10 EFFECT OF PRESSURE ON SELECTIVITY AND ISOMERIZATION

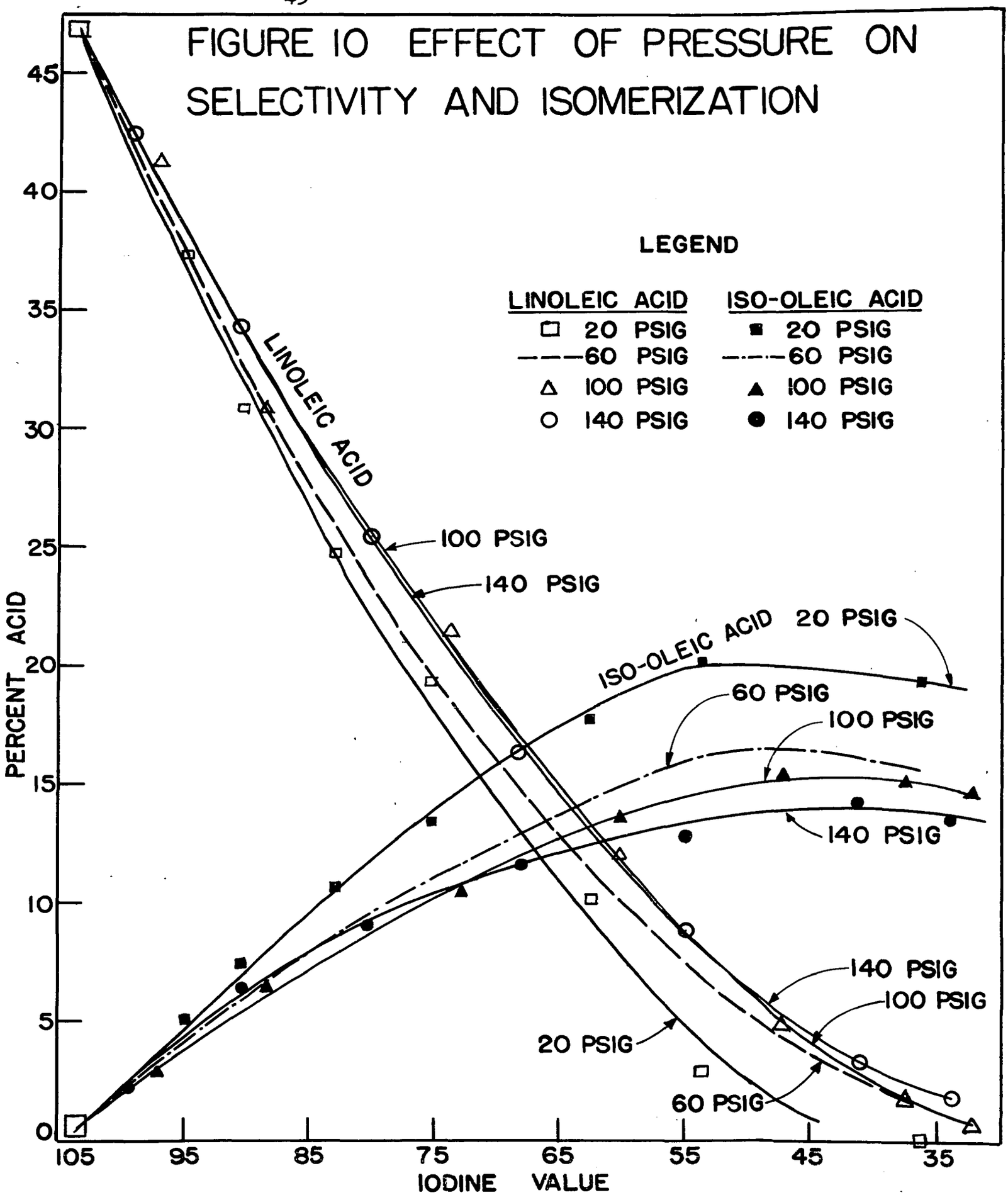


FIGURE 11 EFFECT OF CATALYST CONCENTRATION ON SELECTIVITY AND ISOMERIZATION

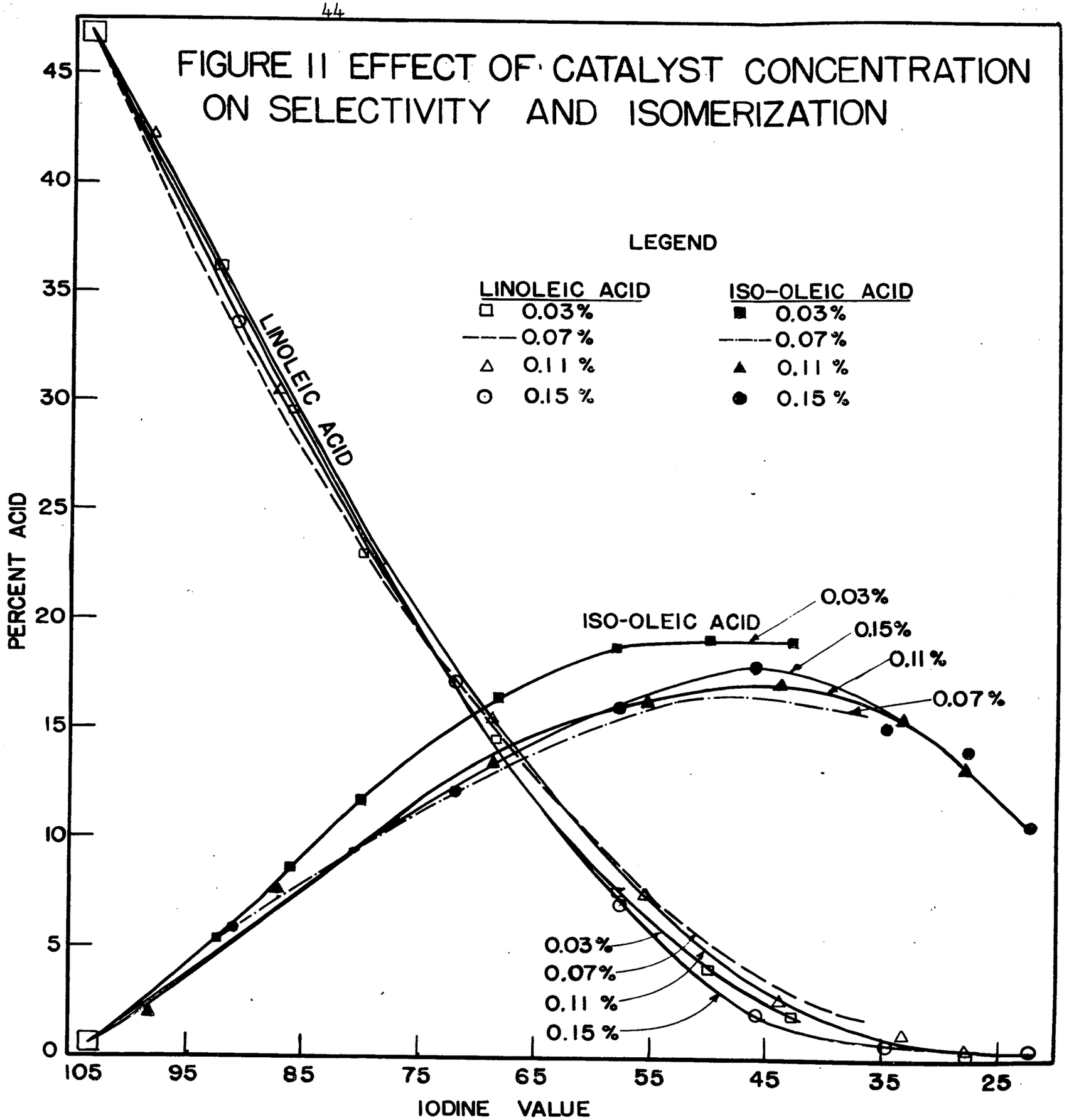
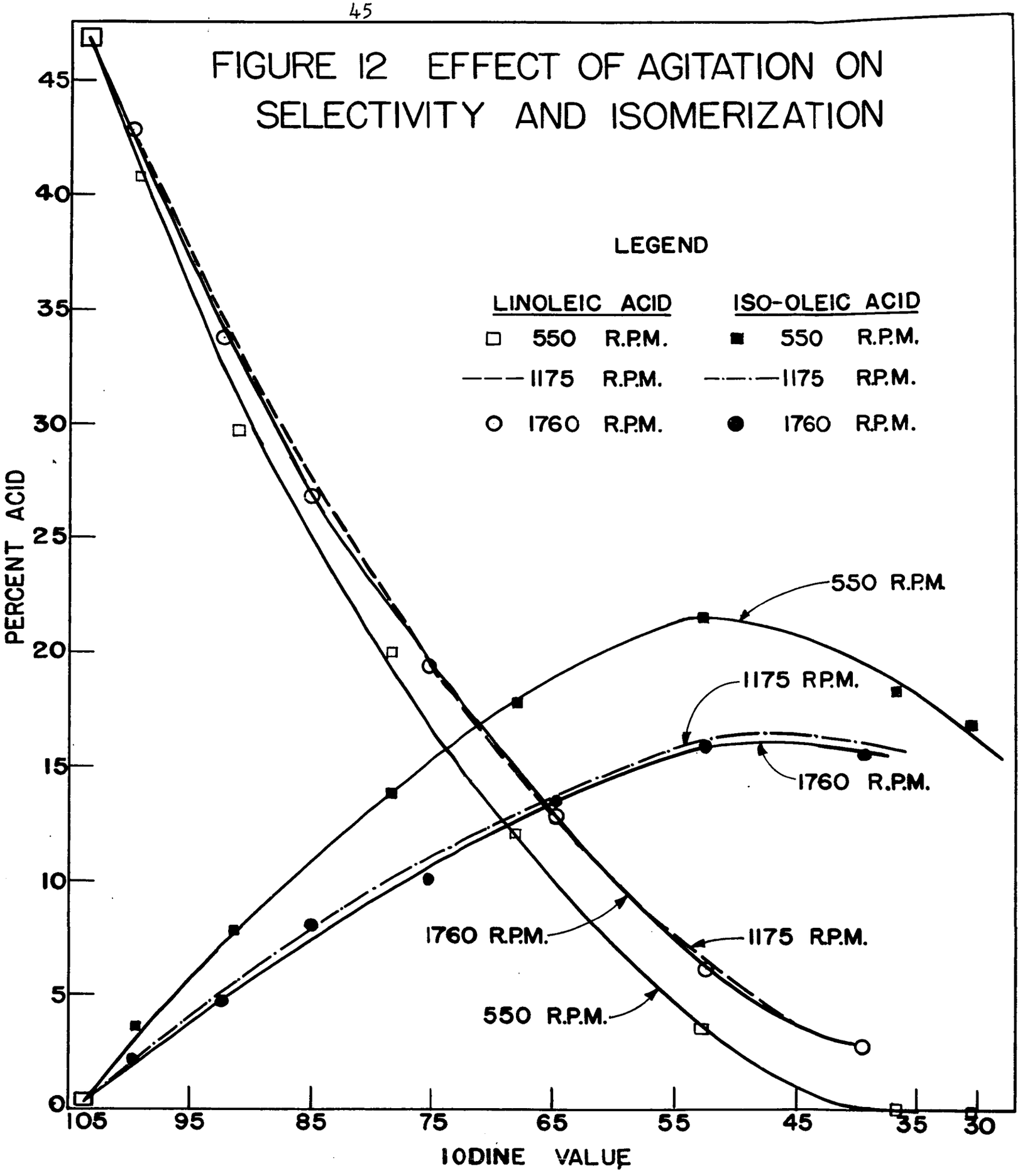


FIGURE 12 EFFECT OF AGITATION ON SELECTIVITY AND ISOMERIZATION



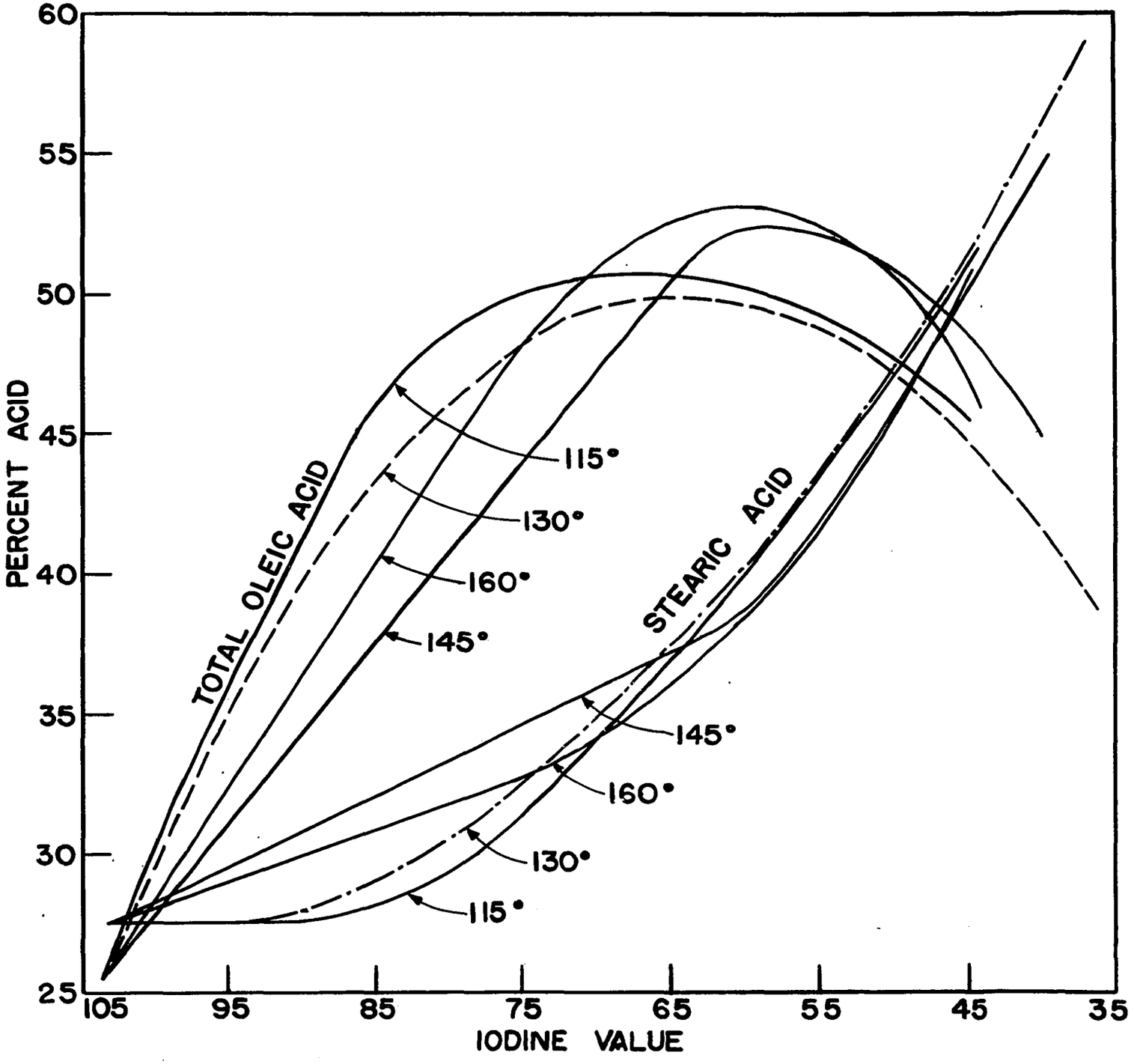


FIGURE 13 EFFECT OF TEMPERATURE ON FORMATION OF TOTAL OLEIC AND STEARIC ACIDS

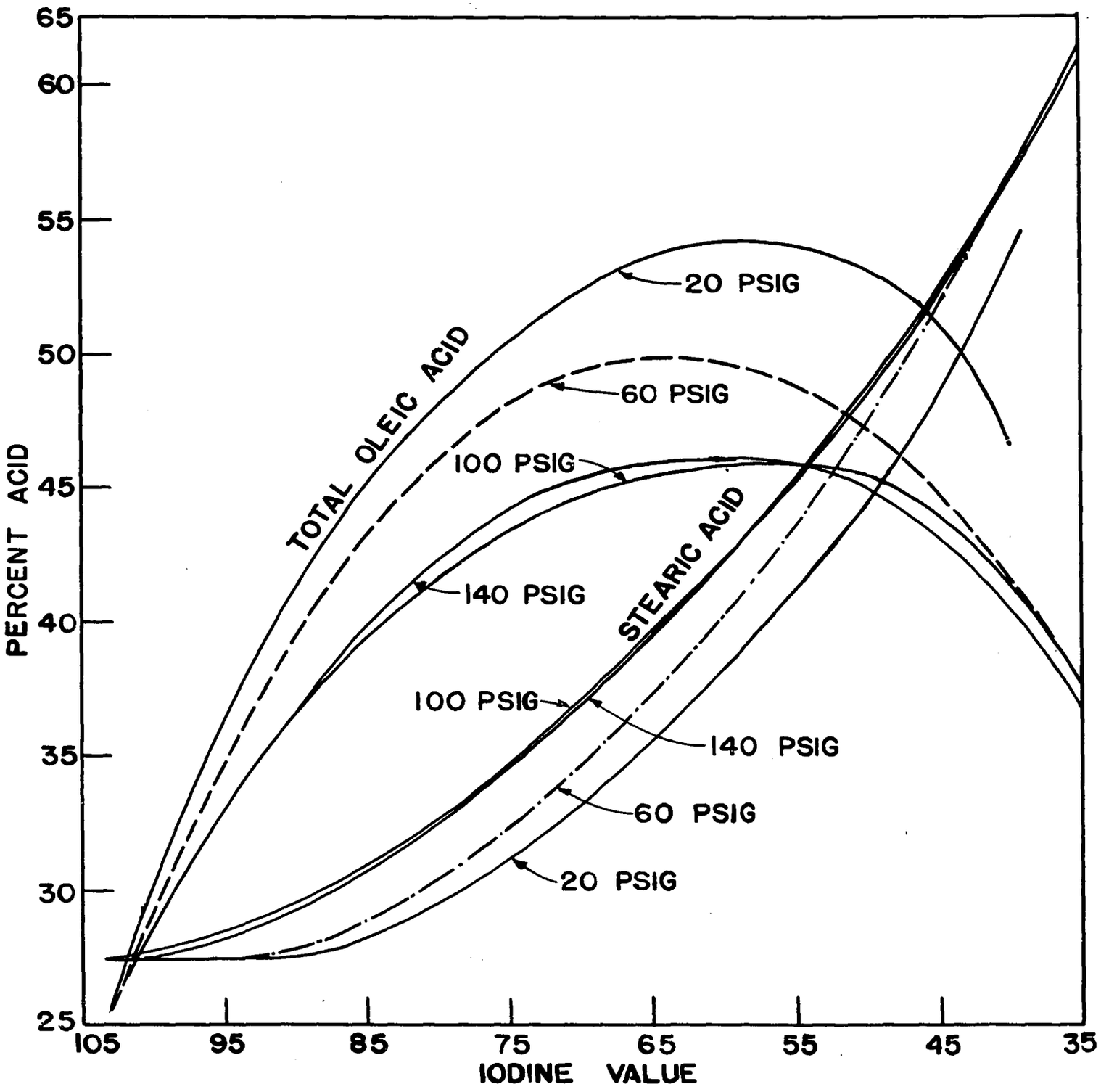


FIGURE 14 EFFECT OF PRESSURE ON FORMATION OF TOTAL OLEIC AND STEARIC ACIDS

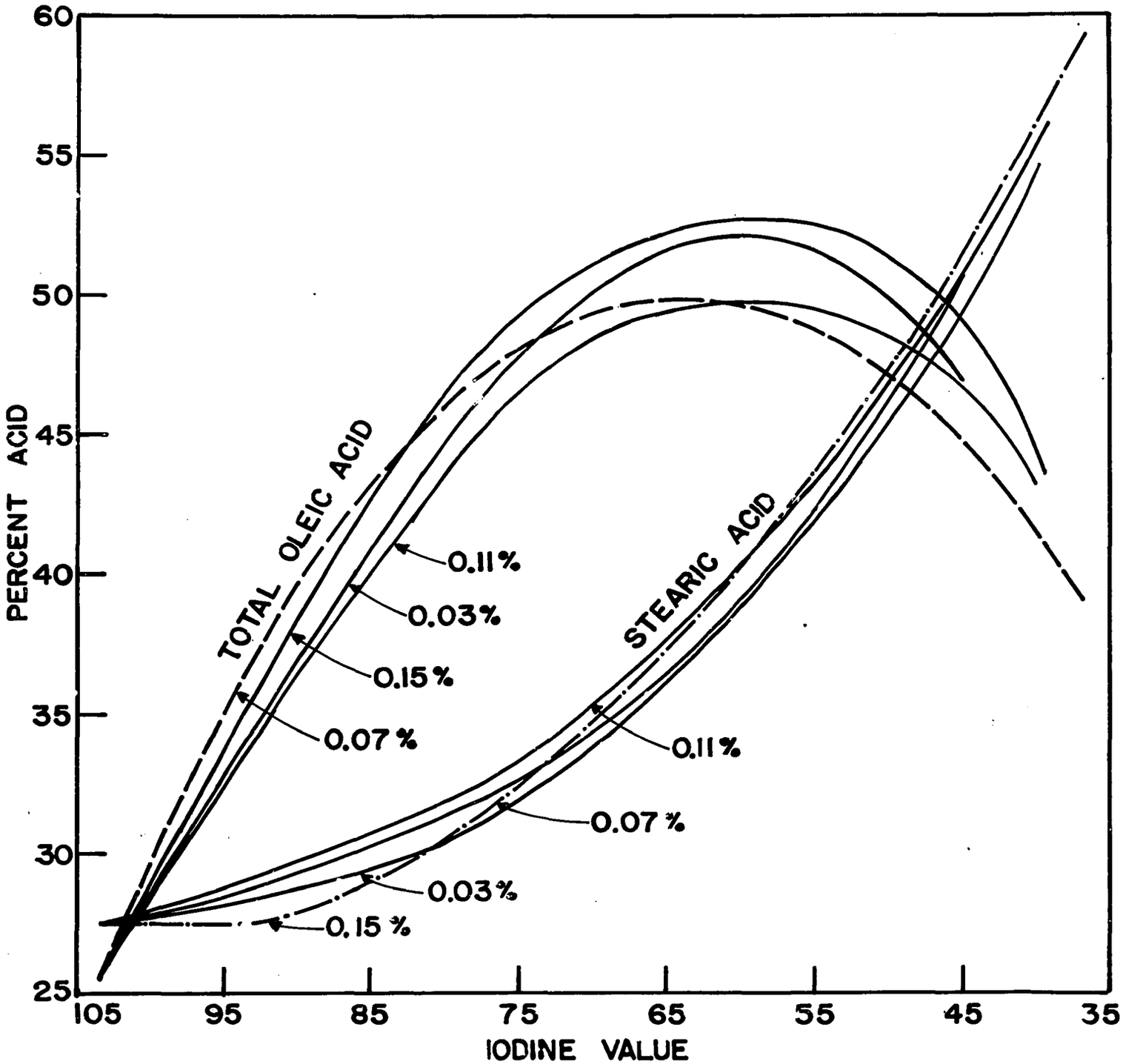


FIGURE 15 EFFECT OF NICKEL CATALYST CONCENTRATION ON FORMATION OF TOTAL OLEIC AND STEARIC ACIDS

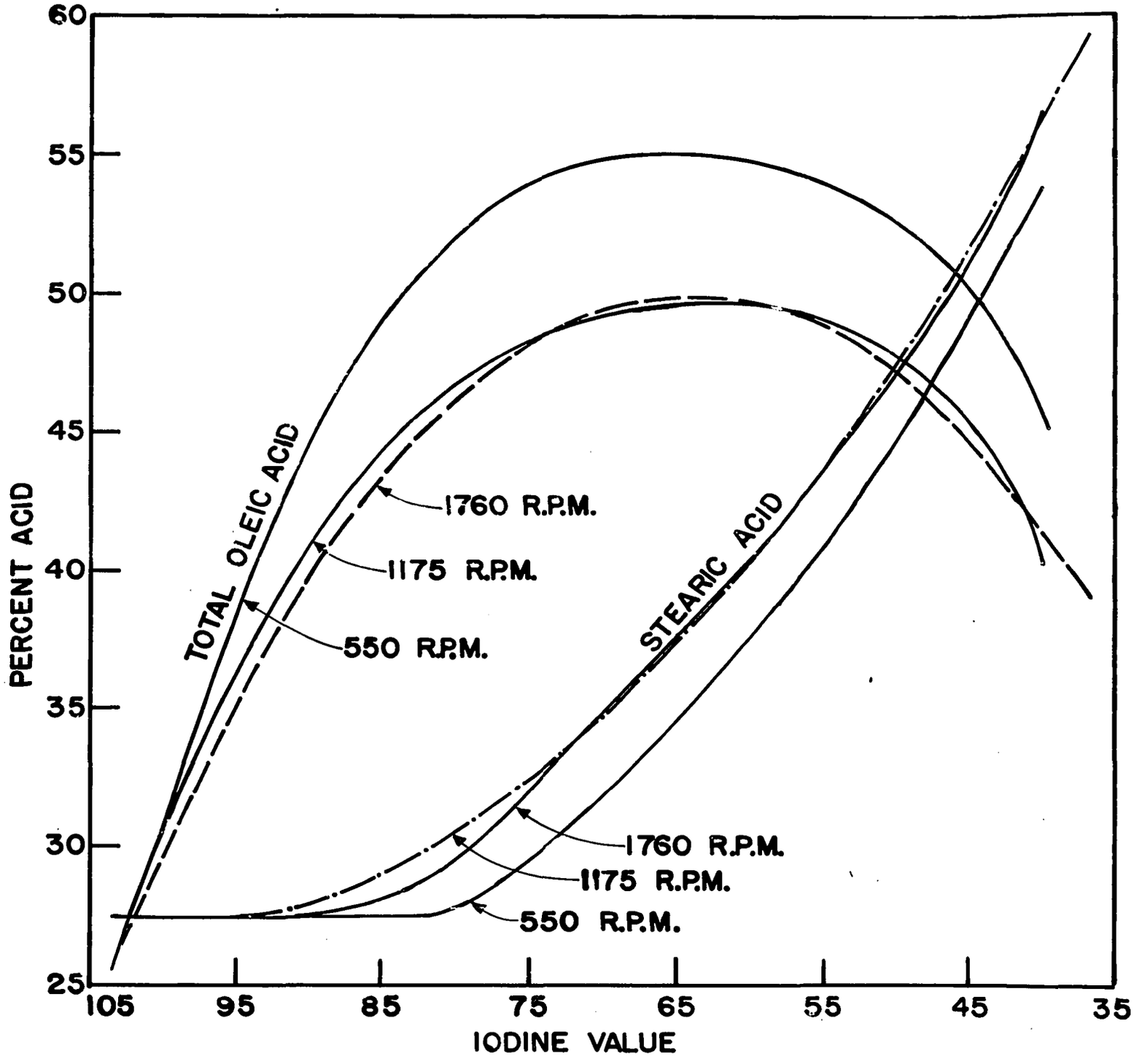


FIGURE 16 EFFECT OF AGITATION ON FORMATION OF TOTAL OLEIC AND STEARIC ACIDS

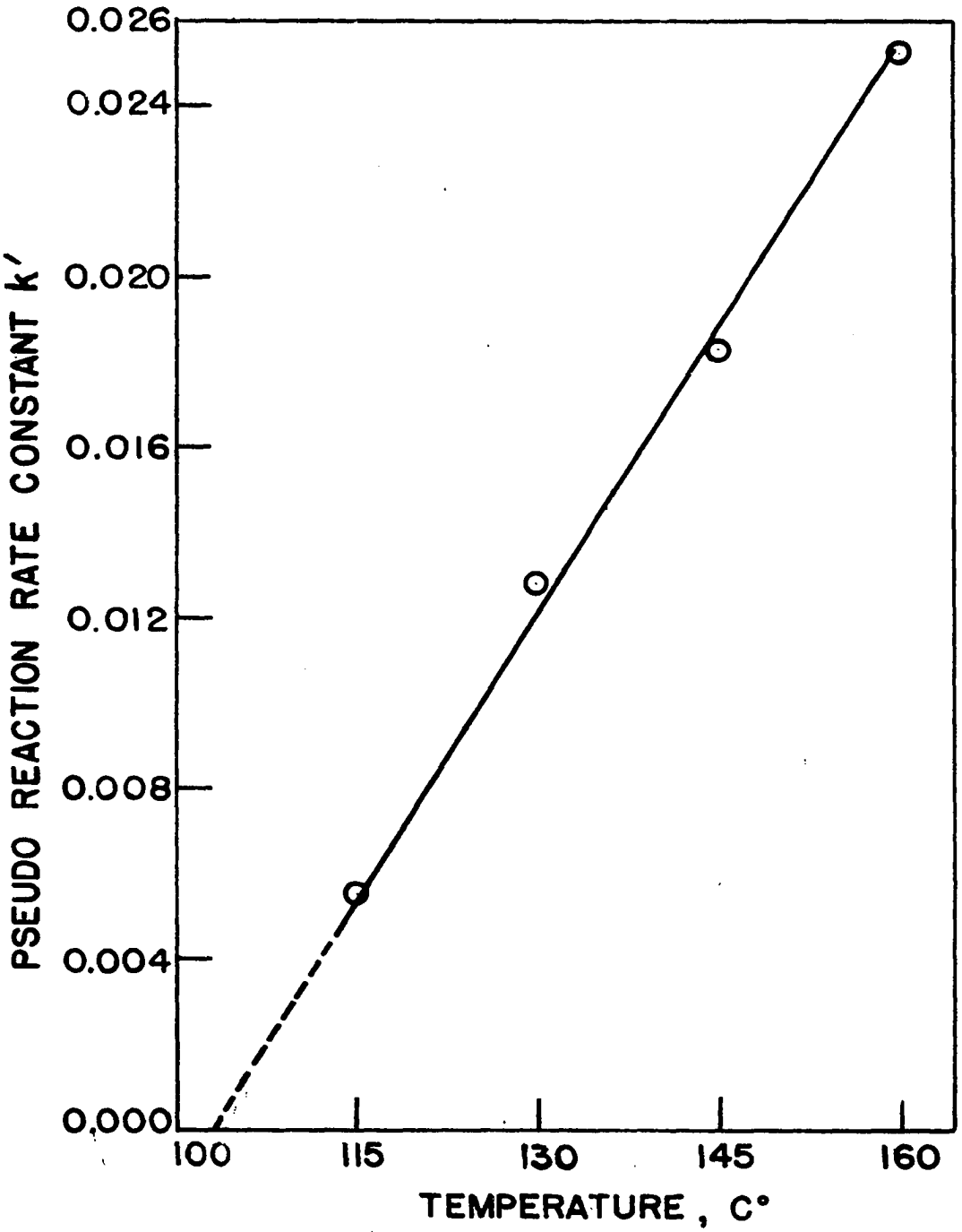


FIGURE 17 EFFECT OF TEMPERATURE ON PSEUDO REACTION RATE CONSTANTS

k' is zero at a temperature of 103°C. Figure 9 indicates that there is relatively little change of selectivity with temperature. More iso-oleic acid is formed, however, at higher temperatures.

Effect of Pressure

The effect of pressure on k' is shown by Figure 18. The values of k' plotted were for runs 1 and 11, 8, 9, and 10. Figure 18 indicates that k' (and consequently the overall rate of hydrogenation) is directly proportional to the absolute pressure. Selectivity and isomerization (as shown in Figure 10) both decrease with an increase in pressure from 20 to 100 psig. The increase in pressure from 100 to 140 psig, however, has only a small effect on either factor.

Effect of Nickel Catalyst Concentration

The hydrogenation rate (as indicated by Figure 19) was found to increase with catalyst concentration and to be directly proportional to it. Values of k' plotted in Figure 19 were for runs 1 and 11, 5, 6 and 7. Selectivity and isomerization (as shown in Figure 11) are not significantly affected by an increase in catalyst concentration. The only exception is the run at low (0.03% nickel) catalyst concentrations. The iso-oleic acid formation of this run was higher than those of the other catalyst runs.

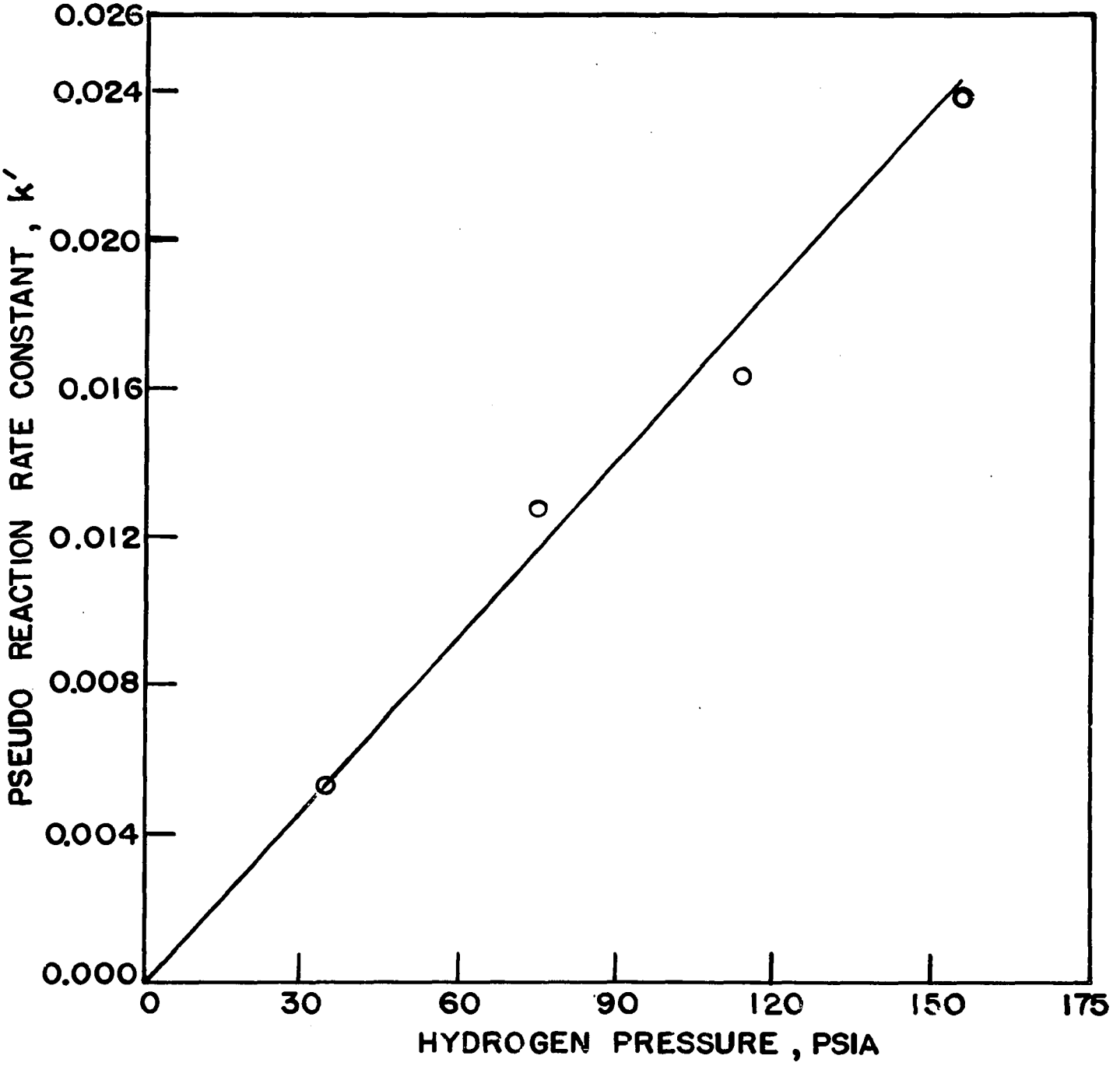


FIGURE 18 EFFECT OF PRESSURE ON PSEUDO REACTION RATE CONSTANTS

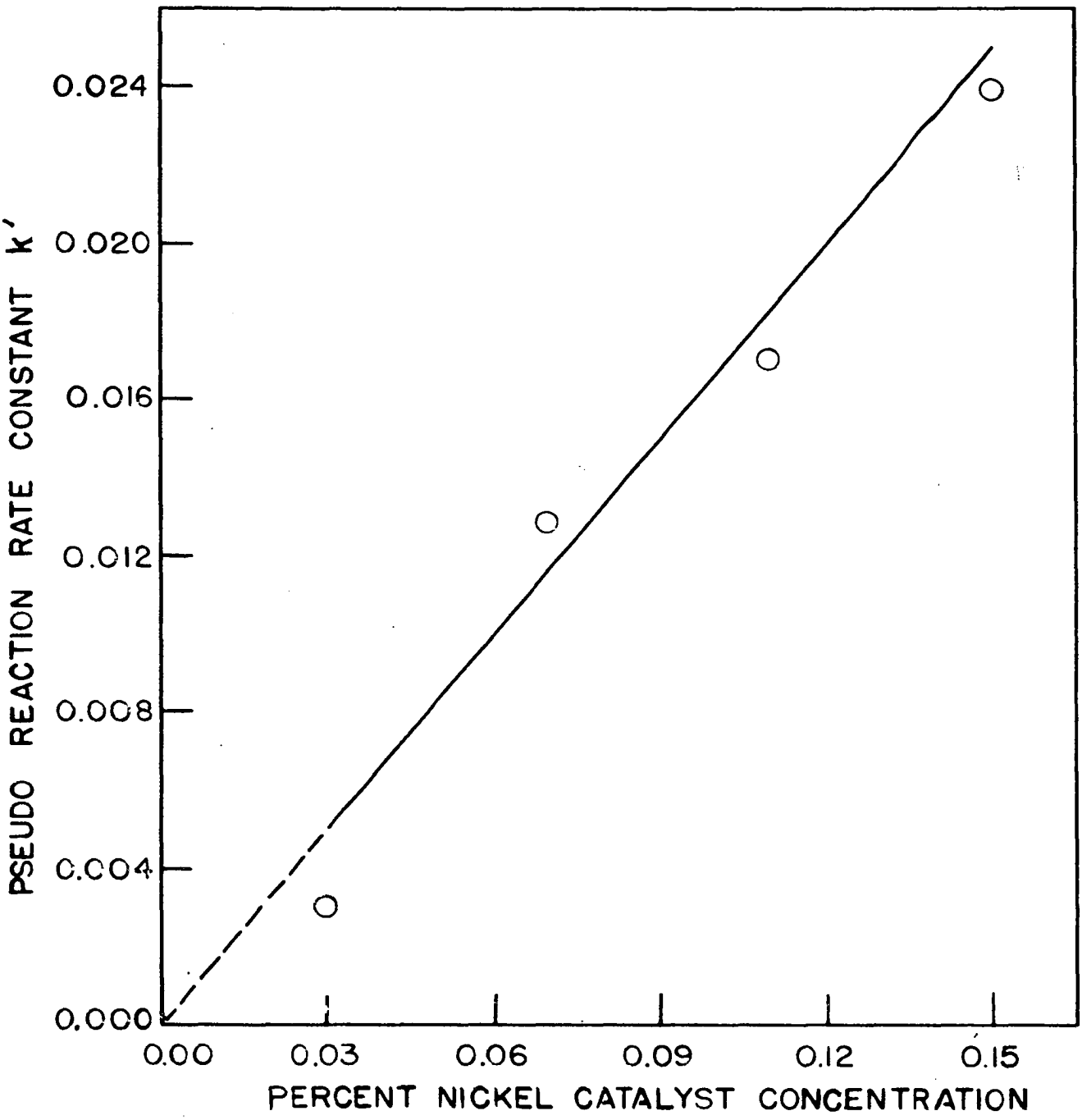


FIGURE 19 EFFECT OF NICKEL CATALYST CONCENTRATION ON PSEUDO REACTION RATE CONSTANTS

Effect of Agitation

The overall rates of hydrogenation for the middle (1175 rpm) and high (1760 rpm) agitation runs, as shown by Figure 7, were almost identical. The low (550 rpm) agitation run, however, results in slower hydrogenation rates. Figure 12 shows that the middle and high agitation have essentially the same effect on selectivity and iso-oleic acid formation. Low agitation, however, results in more selective hydrogenation and increased formation of iso-oleic acid.

Correlation of Data

The following empirical equation was developed to represent the overall rate of hydrogenation at iodine values of 80 or less:

$$r = 0.0000821\ (T-103)(P)(W)(I.V.) \qquad (IV - 3)$$

where

r = I.V. drop per minute

T = temperature, °C

P = absolute hydrogen pressure, psia.

W = weight percent nickel used as catalyst

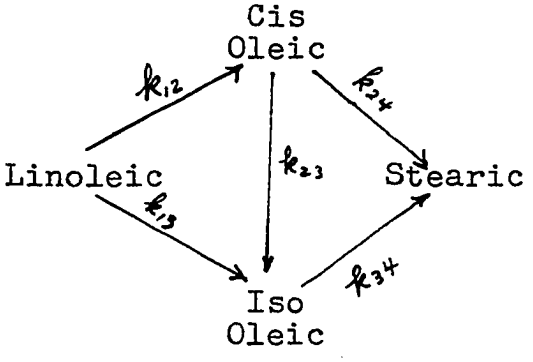
I.V. = iodine value of oil

This equation was developed from the k' values in Table I. It was found to represent the rate of hydrogenation of all runs within 10%, except for the runs at low agitation and with low (0.03% nickel) catalyst. Calculated values of k'

are shown in Table I for each run.

Quantitative Measurements of Selectivity and Isomerization

The main reactions occurring in the hydrogenation of cottonseed oil can be represented schematically as follows:



It was assumed that these steps are irreversible first order reactions and equations were then developed[24] to represent the amount of each acid at any time as a function of original concentrations and of the relative reaction rate constants (k's). The equations so developed are shown in Appendix C. Relative reaction rate constants were calculated for several runs using a trial and error solution and pseudo times of reaction. A sample calculation is shown in Appendix C. The values of k so calculated are shown in Table II. The equations and the calculated k values were found to represent the experimental composition data, in most cases, within experimental accuracy. It should be emphasized that the k values obtained by this method serve only as a quantitative measurement of selectivity and isomerization.

They are not absolute reaction rates, but only indicate the course and relative rates of the various reaction steps.

TABLE II

RELATIVE REACTION RATE CONSTANTS FOR VARIOUS HYDROGENATION RUNS

Run No.	k_{12}	k_{13}	k_{23}	k_{24}	k_{34}
1, 11	0.8	0.20	0.3	0.075	0.60
3	0.55	0.45	0.1	0.1	0.33
5	0.50	0.50	0.15	0.05	0.4
8	1.0	0.0	0.55	0.0	0.6
10	0.65	0.35	0.12	0.24	0.4
12	1.0	0.0	0.46	0.0	0.33

Proposed Mechanism of Reaction

The following mechanism is proposed for the hydrogenation of cottonseed oil as conducted in this research.

(1) The solution of hydrogen into the oil.

(2) The mass transfer of dissolved hydrogen from the bulk liquid phase to the catalyst surface.

(3) The mass transfer of the fatty acids from the bulk liquid phase to the catalyst surface.

(4) The atomically or more probably molecularly chemisorption of hydrogen on the catalyst surface.

(5) The physical adsorption of the fatty acids on the catalyst surface with linoleic being adsorbed preferen-

tially as compared to oleic.

(6) The surface reaction between chemisorbed hydrogen and the physically adsorbed unsaturated fatty acid on the catalyst surface.

(7) The desorption of the hydrogenated fatty acid from the catalyst surface.

(8) The mass transfer of the hydrogenated fat from the catalyst surface to the bulk liquid phase.

It seems probable that the surface reaction (step 6) was controlling in most of the runs made in this investigation.

CHAPTER V

DISCUSSION OF RESULTS

The present data were examined to determine their consistency and accuracy.

The analytical techniques used in the present study are considered accurate within the following limits: iodine values to ± 1 unit, and linoleic acid content to ± 1% acid. This is verified since each sample was run at least twice until two or more consecutive results agreed within the above-mentioned accuracy. In the case of iso-oleic acid, the accuracy was within ± 2% acid. This was verified by frequently running a given sample two or more times. All the analytical procedures used have been recommended by the American Oil Chemists Society.

The iron-constantan thermocouple used to measure the temperature inside the reactor was calibrated at the boiling point of distilled water. It is thought that the readings of the thermocouple as measured in the present research were accurate to ± 1°C. Some difficulty was encountered in maintaining the exact temperature desired during the course of the reaction. Deviations of +5°C were experienced in the

first one or two minutes during the introduction of the catalyst. Deviations up to 2°C were noted during the remaining course of the reaction. These deviations probably affected the results to an insignificant extent since the k' values form a smooth curve when plotted as a function of temperature, as shown in Figure 17.

The pressure gauges used to measure the pressure inside the reactor were calibrated frequently against a dead-weight gauge tester. It is considered that the pressures read were accurate to within ± 1 psig and could be maintained by the pressure regulator within these limits except during sampling. During this period, it may have decreased 5 to 10 psig for about 30 seconds. These pressure deviations, however, are considered to have only a small effect on the reaction since the rate constants correlate well as a function of pressure, as shown in Figure 18.

The agitator speed as reported is considered to be practically constant. This was verified by frequent checks with a tachometer and in no case did it deviate by more than 20 rpm. The inaccuracies in weighing the batch of oil to be hydrogenated were probably less than 0.2%. The amount of nickel catalyst added to the reactor was probably accurate to within 1.0%.

Some errors were introduced in the timing while taking the samples. This is due to the fact that several valves were manipulated, and the lines were flushed with

hydrogen before what was considered to be a reliable sample was obtained. As a result, it is possible that an error as high as ten seconds may have occurred. Such a time factor could mean a change of I.V. up to almost one unit at the faster hydrogenation rates.

Any change of the oil composition from one run to another is considered to be insignificant. The main supply of oil was always kept in a cold room at 49°F. Just prior to a run 1500 grams were drawn from the main batch. The remainder was then left under refrigeration for future use. Over a period of six months the iodine value of the oil was determined several times and varied over a range of 103 to 104 I.V., the linoleic acid content varied from 46.75 to 47.25%, and the iso-oleic acid content was always practically negligible. No consistent changes in these fat samples were ever noted.

The experimental data were, in all cases, consistent, which indicates that the experimental and analytical techniques were also consistent. This is verified by the good reproducibility of the results of the two runs at the average conditions (130°C, 60 psig, 0.07% catalyst and 1175 rpm), see Figure 8. The data for each run were also consistent as indicated by their small deviations from the smoothed curves (see Figures 4 to 7). In addition smooth correlations of the pseudo first order reaction rate constants were obtained as a function of temperature, pressure, and catalyst

concentration (see Figures 17, 18 and 19).

An examination of the results of this research indicates that mass transfer resistances were essentially eliminated in most of the runs. This is demonstrated by the fact that the run at the highest agitation rate (Run 13) did not change the rate or type of hydrogenation as compared to the average runs (Runs 1 and 11) at slower agitation. In addition, mass transfer resistances were at least almost eliminated in the pressure and catalyst runs. This can be proven by the following facts:

(a) Mass transfer of the hydrogen from the gas to the oil phase cannot be controlling, since the rate of hydrogenation is directly proportional to the amount of catalyst.

(b) Mass transfer of the hydrogen from the oil phase to the catalyst surface cannot be controlling, since the rate of hydrogenation for a given run is proportional to the iodine value.

(c) Mass transfer of the unsaturated oil to the catalyst surface cannot be controlling, since the rate of hydrogenation is directly proportional to the absolute hydrogen pressure.

(d) Mass transfer of the saturated oil from the catalyst surface to the main body of oil is not controlling, since the rate of hydrogenation for a given run is proportional to the iodine value.

The rate of hydrogenation in the temperature runs is

similar to those of the pressure or catalyst runs. Therefore, the rate of mass transfer in all runs are comparable. As a result it seems likely that mass transfer resistances in the temperature runs were also eliminated. Another support to this view would be that high temperatures result in lower viscosities and hence probably lower resistances to mass transfer. The low agitation run (550 rpm) is, therefore, probably the only run in which mass transfer resistances are significant.

The present results were compared to similar ones of Bailey[12] and other investigators.[8,9,10,11] Bailey's results are the most recent and complete. Apparently no previous workers eliminated mass transfer resistances in the majority of their runs. The fact that Bailey[12] did not is demonstrated by the continuous increase of his overall hydrogenation rates with increased agitation. The data obtained in the present study agree qualitatively with the findings of Bailey that the overall rate of hydrogenation increases with temperature, pressure, catalyst concentration, and agitation up to 1175 rpm. Quantitatively, the present data agree with the findings of Bailey that the average hydrogenation rates increase as a linear function of temperature. The present results, however, disagree with Bailey since his results do not indicate a linear increase in the overall rate with increases of catalyst concentration or pressure.

Bailey's results further agree with the present

findings that selectivity and isomerization are favored by decrease of pressure and agitation. Bailey's results disagree, however, as to the effect of catalyst concentration on these two factors. His results indicate that selectivity and isomerization increase with catalyst concentration while the data presented here show no appreciable effect of catalyst concentration on either factor. The disagreements between Bailey's results and those presented here are considered to be caused by the following two factors:

(1) Bailey did not eliminate mass transfer in most of his runs.

(2) Bailey used analytical techniques which are less reliable[7,16] than those used in present day studies.

The rate of hydrogenation when defined as iodine value drop per minute per given amount of catalyst is found to be essentially constant (at an I.V. of 80 or less) for the average run (Runs 1 and 11), the highest agitation run (Run 13), and the two higher catalyst runs (Runs 6 and 7). It is noted that selectivity and isomerization are similar in these runs. The rate as defined here was lower for the low catalyst run (Run 5) and the low pressure run (Run 8). In these runs isomerization was appreciably higher than in Runs 1 and 11, 6, 7, and 13. Selectivity was favored for the low pressure run. With the runs at higher pressures (Runs 9 and 10), the rates were higher and selectivity and isomerization were considerably lower. It was found that for

Bailey's results[12] (using a catalyst concentration of 0.05 to 0.1%) when the rate for a given amount of catalyst increased at a given temperature, the selectivity and isomerization always decreased. Therefore, selectivity and isomerization are apparently independent of the catalyst concentration. They depend, however, on the concentration of reactants at the surface and probably on temperature.

The data presented here agree with the findings of Krane[18] in that the overall hydrogenation rate increases with temperature, pressure and catalyst concentration. Krane's results are similar to the present findings in that the hydrogenation rate tends to approach zero at an approximate temperature of 103°C (see Figure 17). His findings also agree with the results of the present data in that raising the pressure not only increases the rate of reaction, but also has a tendency to make the rate more closely approach first order behaviour with respect to concentration of the unsaturate. This is clearly shown in Figure 5 by the linearity of the plot at 140 psig all during the course of the reaction as compared to the linearity of the plot only at an I.V. of 80 or less for lower pressures. Krane, however, did not study selectivity or isomerization. He also did not eliminate mass transfer resistances in his investigation.

The results of the present research also agree with the findings of Zimov'ev[25] that in the hydrogenation of

fats with a reduced nickel formate catalyst, the following is noted:

(a) The change in iodine value with respect to time is proportional to the iodine value of the fat (see equation IV - 3).

(b) The pseudo first order reaction rate constants increase at the beginning of the hydrogenation reaction then become constant (see Figures 4-7).

(c) The hydrogenation rates are proportional to the amount of catalyst in the oil with the rate extrapolating to zero with zero catalyst (see Figure 19).

Zimov'ev, however, did not study in this investigation[25] selectivity, isomerization, or the effects of pressure in hydrogenation of vegetable oils.

Selectivity by definition results in higher reaction rates for linoleic acid than for oleic acid. Assume that the rate of surface reaction for linoleic acid with hydrogen is:

$$r_L = k_L A_L C_{H_2} \qquad (V - 1)$$

and that for oleic acid is

$$r_O = k_O A_O C_{H_2} \qquad (V - 2)$$

where

k_L = reaction velocity constant for linoleic acid

k_O = reaction velocity constant for oleic acid

A_L = concentration of linoleic acid at the catalyst

interface

A_O = Concentration of oleic acid at the catalyst interface

C_{H_2} = Concentration of hydrogen adsorbed on the catalyst surface

The adsorbed hydrogen concentration, C_{H_2}, is constant at a given time for both the linoleic and oleic hydrogenation. Then in order for r_L to be bigger than r_O (i.e., selectivity prevailing), k_L should be bigger than k_O when $A_L = A_O$ or A_L should be bigger than A_O when $k_L = k_O$. It is probable, however, that $k_L = k_O$ because of the constancy of the pseudo reaction rate constant (k') for a given run at an iodine value of 80 or less. It follows then that A_L is probably greater than A_O. This seems to indicate that linoleic acid is preferentially adsorbed to oleic acid. This phenomenon explains selectivity and rules out the possibility of random adsorption of linoleic acid.

In the present results and those of Bailey,[12] increases in selectivity were accompanied by increases in iso-oleic acid formation. If lower hydrogenation rates per given quantity of catalyst resulted in greater selectivity and more isomerization, then the proposed mechanism of preferential adsorption which was used to explain selectivity could possibly be used to explain isomerization. At lower hydrogenation rates more time is available for preferential adsorption on the catalyst surface. When a normal (cis) oleic acid radical is adsorbed on the catalyst surface,

a linoleic acid radical, which is preferentially adsorbed, will tend to replace it. The cis oleic acid will probably be desorbed, if time is available, either by replacement with linoleic acid or by simple desorption without replacement. The latter could be expected to be rather common if the binding forces of the catalyst to the oleic acid are relatively weak. When the oleic acid is desorbed it may be that it isomerizes to iso (trans) oleic acid, which is the geometric isomer. This iso-oleic form is reportedly more stable than the cis form. When the rate of hydrogenation for a given amount of catalyst is high, the adsorption of the unsaturates on the catalyst surface is apparently much more random with regard to linoleic and oleic acids than at slower rates. Consequently less preferential adsorption takes place resulting in lower selectivities and lower iso-oleic acid formation.

The low catalyst run (Run 5) is the only run in which higher iso-oleic acid formation is not accompanied by appreciably higher selectivity. This could be explained by the fact that the amount of hydrogenation performed by a given amount of catalyst is at least twice as much as any other run. Consequently, the increased iso-oleic acid formation noted is probably caused by changes in the catalyst activity due to increased use. The relatively low rates of hydrogenation for this run (see Figure 6) probably are caused mainly by this fact, too. It is possible, however,

that any catalyst poisons in the oil would affect this run to an appreciably higher extent than the other runs.

It is of interest to note that the rate of hydrogenation for most runs is quite low at the start of the run. As the hydrogenation progresses, the rate increases until it is represented essentially by equation (IV - 1). The initial slow hydrogenation is caused probably by trace compounds in the fats such as aldehydes and ketones, etc. These compounds apparently hydrogenate slowly but preferentially to linoleic, oleic, and iso-oleic acids.

The equations developed for expressing the concentration of the various acids as a function of their original concentrations and of the relative reaction velocity constants were used to quantitatively measure selectivity and isomerization. The equations are a continuation of Bailey's[17] work. However, they contain additional terms which were used to quantitatively measure the relative reaction rate constants for the formation of iso-oleic acid. These equations were found to fit the data of several of the runs conducted in the present work. The results indicate as can be seen by the relative reaction rate constants (see Table II) that iso-oleic acid is formed not only by the isomerization of cis-oleic, but is also formed by the hydrogenation of linoleic acid. However, it is noted that linoleic acid, in most cases, hydrogenates predominantly to cis-oleic. In addition, the results indicate that iso-oleic

acid hydrogenates more rapidly than cis-oleic acid. The assumptions made in the derivation of these equations that all steps are irreversible may not be applicable in all cases. This could be especially true in the isomerization step of cis to iso-oleic acid.

The empirical equation

$$\frac{r}{W} = 0.0000821(T-103)\ (P)\ (I.V.) \qquad (V - 3)$$

developed to correlate the present data shows that at constant unsaturation the rate of hydrogenation (at an I.V. of 80 or less) is proportional to the hydrogen pressure. This finding agrees with the results of Wynkoop[19] for the hydrogenation of ethylene over copper-magnesia catalyst, and with those of Sussman et al[20] for the hydrogenation of propylene over a similar catalyst. Similar results were found in the work of Gol'danskii and Elovitch[26] concerning the hydrogenation of oleic acid in both alcohol and acetic acid solutions. In almost all cases the reaction is reported first order with respect to hydrogen and zero order with respect to the oleic acid. This may indicate in that work that mass transfer resistances were significant.

The empirical equation (V - 3) further shows that the hydrogenation rate is zero at a temperature of 103°C. This is also noted in Krane's[18] study which covered the temperature range from 120° to 200°C. This could be attributed to his use of a catalyst similar to that used in the

present work. Equation (V - 3) also shows the hydrogenation rate to increase linearly with temperature. The results of Bailey[12] agree with this finding.

The empirical equation (V - 3) can probably be used to predict rate values in commercial operations within the range of the experimental variables studied here. This should be true if mass transfer resistances are eliminated. The equation should be used with caution if applied beyond the range of operating conditions from which it was developed. It is, however, felt that it can predict with fair accuracy rates in the ranges:

(a) 115 to 200°C. The upper limit seems valid because of Krane's work.

(b) All pressures up to 140 psig.

(c) Up to 0.2% nickel catalyst concentration. This should be true if the catalyst particles are unaffected by each other and if the activity of the catalyst during a run remains unchanged.

Equation (V - 3) could be written at a constant temperature as:

$$\frac{r}{W} = C(P_H)\ (I.V.) \qquad (V - 4)$$

If it is assumed that

(a) Hydrogen behaves essentially as an ideal gas such that the hydrogen pressure equals its activity, or $P_H = A_H$ at standard state unit fugacity.

(b) Iodine value is proportional to the activity of the unsaturate, A_U.

As a result of these assumptions equation (V - 4) can be now written as:

$$\frac{r}{W} = C'(A_H)\ (A_U) \qquad (V - 5)$$

C' does not necessarily have to be an absolute constant, if it deviates with pressure, it decreases very slightly (see Figure 18). C', if it deviates with A_U, will decrease very slightly (see Figures 4-7).

In an effort to propose a reaction mechanism for the hydrogenation of cottonseed oil as conducted in this work a comparison was made between the rate equation (V - 5) developed here and those of Hougen et al[21] for seventeen catalytic mechanisms (see Appendix D, Mechanisms a to q). They assumed that one chemical step is rate controlling. In the present study it can be assumed that the terms involving the reverse reaction drop out of the rate expressions because of the high hydrogenation equilibrium constant. This assumption is supported by indications in the literature[18] that the reverse reaction in the hydrogenation of an olefin or a glyceride is negligible up to temperatures of 200°C. The rate equations then developed by Hougen et al then simplify to take the following general form:

$$r = \frac{\text{Kinetic term}}{\text{Adsorption term}_B} \quad \text{(Driving force term)} \qquad (V - 6a)$$

$$= \frac{B}{(Y)^n} A_H \ \underline{\text{or}}\ \frac{}{(Y)^n} A_U \ \underline{\text{or}}\ \frac{B}{(Y)^n} (A_H)(A_U) \qquad (V - 6b)$$

where

B = Kinetic term; this is a function of the forward rate constant, equilibrium constants and the number of molal active centers per unit mass. This term is constant at a given temperature.

Y = Adsorption term; this is a function of equilibrium constants and activities of reactants, products, and inerts.

A = Driving force term, expressed as activity of reactants, where the subscript H refers to hydrogen and U to the unsaturated component.

In comparing equations (V - 5) and (V - 6a) it could be shown that if $(A_H)(A_U)$ is the driving force then

$$C' = \frac{\text{Kinetic term}}{\text{Adsorption term}} \qquad (V - 7)$$

In comparing the empirical rate equation (V - 5) developed in this work with the rate equations proposed by Hougen et al,[21] mechanisms a, b, e, f, i, l, and q should be eliminated. This is because these mechanisms express the rates as a function of only hydrogen or unsaturate activity. This is not true in case of the data presented here for which the rate equation (V - 5) is a function of both hydrogen pressure and unsaturate concentration per unit mass of catalyst.

All the desorption steps proposed by Hougen et al[21] as possible reaction mechanisms could be eliminated. This is because the adsorption terms contain in the numerator a K' term (i.e., hydrogenation equilibrium constant) multiplied

by the activities of hydrogen and the unsaturate. This means that the adsorption term will increase rapidly with increase of pressure or unsaturation. It will therefore result in smaller C' and smaller rates. This is contrary to what has been found in this work and hence eliminates mechanisms c, g, j, m, and p.

In the case of the mechanisms in which the unsaturate is chemisorbed on the catalyst surface, it is to be expected that the adsorption equilibrium constant for linoleic acid would be bigger than the one for oleic acid. This seems to be verified by the explanation that linoleic acid adsorbs preferentially to oleic acid. It is further postulated that the adsorption equilibrium constant of the stearic would be smaller than that of the oleic due to decreased unsaturation. Then the mechanisms (d, h, and o) could not be used to explain the present data. This is because, as hydrogenation progresses, A_U will decrease and A_S will increase. The net result will be a decrease of the adsorption term, thus an increase in C'. This was earlier shown to be inconsistent with the results of this study.

This leaves the following two mechanisms:

Step k: Reaction between chemisorbed molecular hydrogen and unadsorbed (not chemisorbed) unsaturate where the surface reaction is controlling.

Step n: Reaction between chemisorbed atomic hydrogen and unadsorbed (not chemisorbed) unsaturate

where the surface reaction is rate controlling. If the unsaturate is not chemisorbed, it is improbable that the saturate would be adsorbed to any appreciable extent. Hence K_S (for the saturate) would be small. If $(K_H A_H)$ is also assumed to be small, then either mechanism (k or n) could fit the data of the present investigation. In either of these mechanisms, the adsorption term remains essentially constant or could increase slightly as the hydrogenation progresses or as the hydrogen pressure increases. The increase would probably be greater in the case of atomically adsorbed hydrogen since the adsorption term is squared. Since C' in equation (V - 5) should remain constant or could decrease slightly as previously explained, the mechanism of reaction between molecularly adsorbed hydrogen and unsaturate in the fluid phase with the surface reaction controlling is the one proposed to explain the hydrogenation data obtained here. Since the mechanism proposed here indicates that the unsaturate is not chemisorbed and since selectivity and isomerization mechanisms indicate preferential adsorption of linoleic relative to oleic, it seems probable that the preferential adsorption is physical in nature rather than chemical. Krane[18] has proposed a mechanism similar to this presented here for the liquid phase hydrogenation of ethyl oleate. The similarity of the feed, catalyst, equipment, and operating conditions used here with those used by Krane could account for the similarity of his mechanism to

that proposed here.

The mechanism proposed from these data for the hydrogenation of cottonseed oil is only probable. It could not be definitely proved because the work done here does not provide enough data to establish a conclusive mechanism. The results presented here were limited by a prevailing low selectivity because of the elimination of mass transfer resistances. It is thought that this work has, however, thrown considerable light on hydrogenation mechanisms in heterogeneous systems. It could be followed up with more assurances than previously for the purpose of arriving at a more conclusive mechanism.

CHAPTER VI

CONCLUSIONS

In the hydrogenation of cottonseed oil under variable operating conditions (temperature of 115 to 160°C, hydrogen pressure of 20 to 140 psig, commercial Harshaw nickel catalyst concentration of 0.03 to 0.15% and agitation from 550 rpm to 1760 rpm) the following results were obtained:

1. Overall hydrogenation rate can be correlated within 10% by:

$r = 0.0000821(\text{Iodine Value})(P_H, \text{psia})(T^{\circ}C-103)(\%Ni \text{ by weight})$

at 80 I.V. or less when mass transfer resistances are eliminated.

2. Mass transfer resistances were eliminated in most of the hydrogenation runs made in this study. This allowed for a better insight into the reaction mechanism.

3. The empirical equation presented here does not predict rate data for low agitation (Run 12) since mass transfer resistances were not eliminated. It also does not predict rate data for the low catalyst concentration (Run 5) since the activity of the catalyst probably changes during

the run.

4. The empirical equation does not predict rate data at iodine values of 80 or more for most of the runs. This is attributed to the presence of trace compounds (e.g. aldehydes, ketones, etc.) which hydrogenate slower than linoleic or oleic acid but preferential to either one.

5. Selectivity and iso (trans) oleic acid formation are decreased with increased operating pressure. They are also decreased with increased agitation until mass transfer resistances are eliminated.

6. Selectivity and iso (trans) oleic acid formation are not affected by changes in catalyst concentration as long as the catalyst maintains its activity and mass transfer resistances are negligible.

7. Selectivity is not significantly affected by increase in temperature. Iso-oleic acid formation, however, is favored by temperature increases.

8. Selectivity and isomerization result from physical adsorption of linoleic acid on the catalyst surface preferentially to oleic acid.

9. In several runs a quantitative measurement of selectivity and isomerization was made using relative reaction rate constants.

10. A mechanism was proposed for the hydrogenation reaction. The surface reaction step between chemisorbed

hydrogen and physically adsorbed unsaturate appeared to be rate controlling. This mechanism is similar to that proposed by Krane[18] for the hydrogenation of ethyl oleate.

APPENDIX A

ANALYTICAL RESULTS OF EXPERIMENTAL RUNS

TABLE III

Run 1. at 130°C, 60 psig, 0.07% Ni, and 1175 rpm

Sample No.	Time in Minutes	Iodine Value	% Linoleic Acid	% Iso-oleic Acid
1	15	102.60	44.30	2.12
2	30	93.55	35.30	5.03
3	45	76.15	21.15	11.60
4	60	64.80	12.95	13.80
5	75	51.40	6.19	17.05
6	90	40.70	3.37	16.82
7	105	35.00	2.23	16.05

TABLE IV

Run 2. at 145°C, 60 psig, 0.07% Ni, and 1175 rpm

1	7	95.55	39.50	2.29
2	14	83.45	28.10	7.87
3	21	68.55	16.53	12.12
4	28	60.75	9.08	14.88
5	35	52.05	4.61	17.07
6	44	44.80	1.91	17.00
7	53	38.00	0.68	15.00

TABLE V

Run 3. at 160°C, 60 psig, 0.07% Ni, and 1175 rpm

1	7	85.50	29.65	8.02
2	11	75.70	20.25	12.18
3	15	67.70	14.08	15.53
4	19	62.80	9.82	15.95
5	23	57.90	6.92	19.33
6	29	49.75	4.23	19.65
7	34	44.50	2.37	21.35

TABLE VI

Run 4. at 115°C, 60 psig, 0.07% Ni, and 1175 rpm

Sample No.	Time in Minutes	Iodine Value	% Linoleic Acid	% Iso-oleic Acid
1	30	99.70	42.20	1.99
2	60	91.00	32.85	5.92
3	90	80.55	29.48	8.53
4	120	67.40	14.70	11.37
5	150	57.50	7.80	15.13
6	180	47.30	4.50	15.95
7	210	41.60	2.15	15.17

TABLE VII

Run 5. at 130°C, 60 psig, 0.03% Ni, and 1175 rpm

1	60	92.30	36.25	5.31
2	90	85.95	29.60	8.52
3	120	79.65	23.05	11.74
4	165	68.05	14.53	16.34
5	225	57.95	7.58	18.68
6	285	49.95	4.09	19.10
7	375	42.90	1.95	19.00

TABLE VIII

Run 6. at 130°C, 60 psig, 0.11% Ni, and 1175 rpm

1	12	98.25	42.20	1.94
2	24	87.05	30.55	7.58
3	36	68.50	15.40	13.40
4	48	55.20	7.40	16.24
5	63	43.90	2.55	17.05
6	78	33.32	1.03	15.45
7	96	27.72	0.43	13.28

TABLE IX

Run 7. at 130°C, 60 psig, 0.15% Ni, and 1175 rpm

Sample No.	Time in Minutes	Iodine Value	% Linoleic Acid	% Iso-oleic Acid
1	10	90.80	33.60	5.78
2	20	71.75	17.10	12.05
3	30	57.60	6.90	15.90
4	40	45.75	1.85	17.86
5	52	34.55	0.60	15.00
6	60	27.80	0.40	13.98
7	68	22.35	0.30	10.63

TABLE X

Run 8. at 130°C, 20 psig, 0.07% Ni, and 1175 rpm

1	30	94.95	37.40	5.00
2	45	90.37	30.90	7.46
3	60	82.95	24.75	10.71
4	75	75.20	19.30	13.43
5	105	62.50	10.12	17.74
6	150	53.85	2.96	20.10
7	210	36.40	0.00	19.32

TABLE XI

Run 9. at 130°C, 100 psig, 0.07% Ni, and 1175 rpm

1	10	97.00	41.40	2.93
2	20	88.42	30.75	6.51
3	30	73.77	21.47	10.54
4	42	60.10	12.10	13.60
5	57	47.10	4.93	15.35
6	73	37.40	1.93	15.10
7	83	32.27	1.20	14.60

TABLE XII

Run 10. at 130°C, 140 psig, 0.07% Ni, and 1175 rpm

Sample No.	Time in Minutes	Iodine Value	% Linoleic Acid	% Iso-oleic Acid
1	10	99.20	42.40	2.17
2	17	90.30	34.20	6.30
3	24	80.15	25.30	9.06
4	31	68.05	16.36	11.60
5	40	54.90	8.81	12.75
6	52	41.20	3.42	14.18
7	60	33.97	1.91	13.54

TABLE XIII

Run 11. at 130°C, 60 psig, 0.07% Ni, and 1175 rpm

1	15	100.30	42.06	0.59
2	30	92.35	35.70	4.21
3	45	79.90	22.05	9.62
4	60	66.35	13.27	13.34
5	75	54.40	6.81	15.43
6	90	45.90	3.31	16.15
7	105	38.80	1.60	15.44

TABLE XIV

Run 12. at 130°C, 60 psig, 0.07% Ni, and 550 rpm

1	30	99.15	40.90	3.58
2	60	91.15	29.80	7.76
3	90	78.50	20.10	13.84
4	120	68.00	12.00	17.75
5	165	52.70	3.52	21.48
6	225	36.70	0.00	18.24
7	255	30.20	0.00	16.74

TABLE XV

Run 13. at 130°C, 60 psig, 0.07% Ni, and 1760 rpm

Sample No.	Time in Minutes	Iodine Value	% Linoleic Acid	% Iso-oleic Acid
1	13	99.70	42.90	2.01
2	26	92.30	33.75	4.69
3	37	85.00	26.85	8.07
4	48	75.10	19.37	10.00
5	62	64.60	12.80	13.40
6	79	52.30	6.02	15.90
7	99	39.30	2.74	15.55

APPENDIX B

SMOOTHED ANALYTICAL DATA OF EXPERIMENTAL RUNS

TABLE XVI

Average of Runs 1 and 11:

at 130°C, 60 psig, 0.07% Ni, and 1175 rpm

Smoothed Iodine Value	% Linoleic Acid	% Iso-oleic Acid	% Total Oleic Acid	% Stearic Acid
101.2	44.40	1.60	28.30	27.10
93.5	35.70	4.60	36.75	27.75
79.6	23.00	9.70	46.20	30.80
64.5	12.50	13.80	49.80	37.70
52.6	6.50	16.40	48.20	45.30
43.5	3.30	16.30	43.90	52.80
36.6	1.85	15.80	38.90	59.25

TABLE XVII

Run 2. at 145°C, 60 psig, 0.07% Ni, and 1175 rpm

100	43.70	1.40	28.40	27.90
90	34.90	4.60	34.45	30.65
80	26.00	8.35	40.65	33.35
70	17.10	11.50	47.00	35.90
60	9.20	15.20	52.45	38.35
50	3.65	17.10	50.70	45.65
40	0.80	15.60	44.90	54.30

TABLE XVIII

Run 3. at 160°C, 60 psig, 0.07% Ni, and 1175 rpm

100	43.60	2.10	28.60	27.80
90	34.00	6.35	36.20	29.80
80	24.30	10.40	43.70	31.70
70	15.20	14.50	50.80	34.00
60	8.25	17.80	53.15	38.65
50	3.60	20.40	50.90	45.50
45	2.75	21.30	46.85	50.40

TABLE XIX

Run 4. at 115°C, 60 psig, 0.07% Ni, and 1175 rpm

Smoothed Iodine Value	% Linoleic Acid	% Iso-oleic Acid	% Total Oleic Acid	% Stearic Acid
100	42.60	1.80	30.40	27.00
90	31.50	5.30	41.20	27.30
80	22.00	8.80	48.65	29.35
70	15.20	11.90	50.70	34.10
60	9.80	14.60	50.10	40.10
50	5.30	15.90	47.70	47.00
45	3.40	15.80	45.45	51.15

TABLE XX

Run 5. at 130°C, 60 psig, 0.03% Ni, and 1175 rpm

100	43.50	2.00	28.65	27.85
90	33.70	6.60	36.90	29.40
80	23.90	11.70	44.85	31.25
70	15.50	15.70	50.20	34.30
60	8.80	18.35	52.10	39.10
50	4.10	19.10	49.90	46.00
45	2.5	19.00	46.70	50.80

TABLE XXI

Run 6. at 130°C, 60 psig, 0.11% Ni, and 1175 rpm

100	43.70	1.80	28.30	28.00
90	33.90	5.40	36.40	29.70
80	24.50	9.55	43.70	31.80
70	16.35	13.40	48.50	35.15
60	9.90	15.65	49.70	40.40
50	4.70	16.80	48.65	46.65
40	1.70	16.70	43.10	55.20

TABLE XXII

Run 7. at 130°C, 60 psig, 0.15% Ni, and 1175 rpm

Smoothed Iodine Value	% Linoleic Acid	% Iso-oleic Acid	% Total Oleic Acid	% Stearic Acid
100	43.35	2.00	28.95	27.70
90	32.90	5.60	38.30	28.80
80	23.15	9.45	46.40	30.45
70	15.00	12.85	51.15	33.85
60	8.50	15.65	52.70	38.80
50	3.40	17.40	51.30	45.30
40	1.00	17.30	44.50	54.50

TABLE XXIII

Run 8. at 130°C, 20 psig, 0.07% Ni, and 1175 rpm

100	42.30	2.2	30.90	26.80
90	31.35	7.2	41.50	27.15
80	22.10	11.8	48.20	29.60
70	14.35	15.75	52.40	33.25
60	7.70	18.85	54.20	38.10
50	2.45	20.00	53.20	44.45
40	0.00	19.60	46.50	53.50

TABLE XXIV

Run 9. at 130°C, 100 psig, 0.07% Ni, and 1175 rpm

95	38.20	3.80	33.55	28.25
85	29.40	7.05	39.65	30.95
75	21.70	10.10	43.48	34.82
65	15.00	12.70	45.35	39.65
55	9.00	14.55	45.90	45.10
45	4.10	15.30	43.10	52.80
35	1.50	15.00	37.70	60.80

TABLE XXV

Run 10. at 130°C, 140 psig, 0.07% Ni, and 1175 rpm

Smoothed Iodine Value	% Linoleic Acid	% Iso-oleic Acid	% Total Oleic Acid	% Stearic Acid
95	38.20	4.15	33.55	28.25
85	29.30	7.95	39.80	30.90
75	21.50	10.30	43.90	34.60
65	14.70	12.00	45.90	39.40
55	9.00	13.30	45.90	45.10
45	4.70	14.00	43.00	52.30
35	2.00	13.65	36.70	61.30

TABLE XXVI

Run 12. at 130°C, 60 psig, 0.07% Ni, and 550 rpm

100	42.50	2.80	30.75	26.75
90	29.90	8.30	44.45	26.45
80	20.30	13.20	52.05	27.65
70	13.20	17.10	54.80	32.00
60	7.40	20.20	54.85	37.75
50	3.50	21.50	52.70	44.60
40	0.40	19.60	45.70	53.90

TABLE XXVII

Run 13. at 130°C, 60 psig, 0.07% Ni, and 1175 rpm

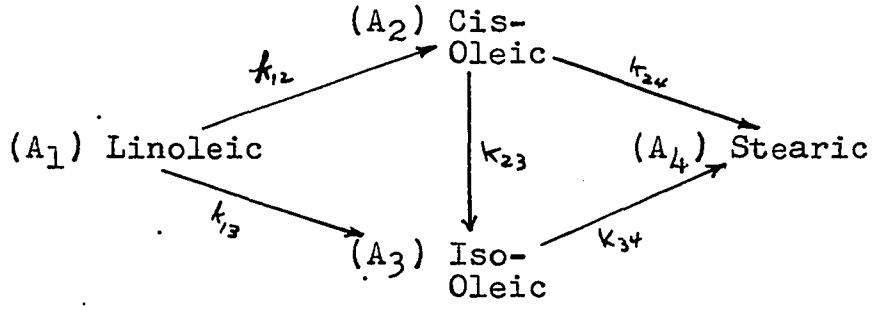
100	42.70	1.9	30.30	27.00
90	31.60	5.7	41.08	27.32
80	22.9	9.05	46.90	29.20
70	16.00	12.10	49.20	34.80
60	10.00	14.5	49.65	40.35
50	5.20	15.8	47.70	47.10
40	3.00	15.5	40.50	56.50

APPENDIX C

EXPRESSIONS FOR QUANTITATIVE MEASUREMENT OF SELECTIVITY AND ISOMERIZATION

APPENDIX C

The reactions occurring during the hydrogenation of cottonseed oil containing linoleic, cis-oleic, iso-oleic and stearic acids could be represented by a series of simultaneous and consecutive reactions. These are schematically presented as follows:



If each of these steps can be represented by a first order irreversible reaction, then the amount of each acid present at any time can be expressed as a function of original concentrations, A^o, pseudo times and relative reaction rate constants.[24] The equations are as follows:

$$A_1 = A_1^o \, e^{-(k_{12}+k_{13})t} \qquad (1)$$

$$A_2 = A_1^o \frac{k_{12}}{(k_{23}+k_{24})-(k_{12}+k_{13})} \left[e^{-(k_{12}+k_{13})t} - e^{-(k_{23}+k_{24})t} \right] + A_2^o \, e^{-(k_{23}+k_{24})t} \qquad (2)$$

$$A_3 = A_1^o \frac{k_{13}(k_{23}+k_{24}-k_{12}-k_{13})+k_{12}k_{23}}{(k_{23}+k_{24}-k_{12}-k_{13})(k_{34}-k_{12}-k_{13})}\left[e^{-(k_{12}+k_{13})t} - e^{-(k_{34})t}\right]$$

$$+ A_1^o \frac{k_{12}k_{23}}{(k_{23}+k_{24}-k_{12}-k_{13})(k_{34}-k_{23}-k_{24})}\left[e^{-k_{34}t} - e^{-(k_{23}+k_{24})t}\right]$$

$$+ A_2^o \frac{k_{23}}{(k_{34}-k_{23}-k_{24})}\left[e^{-(k_{23}+k_{24})t} - e^{-k_{34}t}\right] + A_3^o\, e^{-k_{34}t} \qquad (3)$$

$A_1 + A_2 + A_3 + A_4 = 1.0$, hence A_4 is solved for by difference.

Sample Calculation of the Relative Reaction Rate Constants for the Average Run (Runs 1 and 11)

(1) Assume $k_{12} + k_{13} = 1.0$

(2) Using equation 1, calculate the pseudo times for different iodine values, this equals $\ln \frac{A_o}{A}$

Iodine Value	% Linoleic Acid	Pseudo Time
101.2	44.40	0.0564
93.5	35.70	0.275
79.6	23.00	0.715
64.5	12.50	1.324
52.6	6.50	1.980
43.5	3.30	2.660
36.6	1.85	3.165

(3) Assume a value for k_{12}, also assume a value for $(k_{23} + k_{24})$. Calculate the cis-oleic acid from equation 2. Repeat both assumptions until the calculated cis-oleic acid agrees with its actual value at the different iodine values chosen along the course of the hydrogenation reaction.

These experimental values are the differences between the total oleic and iso-oleic acids at a chosen iodine value. By a trial and error solution the final $k_{12} = 0.8$ and $k_{23} + k_{24} = 0.375$. This gives good agreement with the actual data as shown here:

Iodine Value	Pseudo Time	%(Cis-oleic) calculated	%(Cis-oleic) actual
101.2	0.0564	27.01	26.70
93.5	0.275	31.65	32.15
79.6	0.715	34.91	36.50
64.5	1.324	35.88	36.00
52.6	1.980	32.44	31.80
43.5	2.660	27.27	27.60
36.6	3.165	23.60	23.10

(4) With $k_{12} = 0.8$, $k_{13} = 0.2$, $k_{23} + k_{24} = 0.375$, assume a value for k_{23}, also for k_{34}. Calculate A_3 from equation 3. Repeat the assumptions for k_{23} and k_{34} until the calculated iso-oleic agrees with the actual values. By a trial and error solution the final $k_{23} = 0.3$ and $k_{34} = 0.6$. This gives good agreement with the experimental data as shown here:

Iodine Value	Pseudo Time	%(Iso-oleic) calculated	%(Iso-oleic) actual
101.2	0.0564	1.295	1.60
93.5	0.275	4.66	4.70
79.6	0.715	9.69	9.70
64.5	1.324	14.39	13.80
52.6	1.980	16.09	16.40
43.5	2.660	16.37	16.30
36.6	3.165	15.47	15.80

In order to obtain an overall good agreement between the calculated and the actual values for the various acids it is

sometimes necessary to change slightly the pseudo times. In the case of the average run (Runs 1 and 11) no such adjustment was necessary; therefore the calculated values of linoleic acid were equal to the actual values. From the calculations shown above the values for $k_{12} = 0.8$, $k_{13} = 0.2$, $k_{23} = 0.3$, $k_{24} = 0.075$, and $k_{34} = 0.6$.

TABLE XXVIII

CALCULATED VALUES FOR ACIDS DURING HYDROGENATION USING EQUATIONS 1, 2, AND 3 IN APPENDIX C

Run 3. at 160°C, 60 psig, 0.07% Ni, and 1175 rpm

$k_{12} = 0.55$, $k_{13} = 0.45$, $k_{23} = 0.10$, $k_{24} = 0.10$, $k_{34} = 0.33$

Iodine Value	%Linoleic calc.	%Linoleic actual	%Cis-oleic calc.	%Cis-oleic actual	%Iso-oleic calc.	%Iso-oleic actual
95	38.80	38.80	28.81	28.6	4.75	4.20
90	34.00	34.00	30.85	29.85	6.90	6.35
80	24.50	24.30	33.97	33.60	11.6	10.40
70	15.30	15.20	35.69	37.40	15.6	14.50
60	8.00	8.25	35.07	35.35	18.2	17.80
50	3.67	3.60	32.18	30.50	19.7	20.40
45	2.54	2.75	30.48	25.55	18.4	21.30

TABLE XXIX

Run 5. at 130°C, 60 psig, 0.03% Ni, and 1175 rpm

$k_{12} = 0.5$, $k_{13} = 0.5$, $k_{23} = 0.15$, $k_{24} = 0.05$, $k_{34} = 0.40$

Iodine Value	%Linoleic calc.	%Linoleic actual	%Cis-oleic calc.	%Cis-oleic actual	%Iso-oleic calc.	%Iso-oleic actual
95	38.80	38.80	28.60	28.6	4.99	4.20
90	33.70	33.70	30.30	30.3	7.80	6.60
80	23.90	23.90	33.1	33.1	12.87	11.70
70	15.50	15.50	34.3	34.5	16.62	15.70
60	8.80	8.80	33.8	33.7	18.90	18.35
50	3.98	4.10	31.1	30.8	19.44	19.10
45	2.02	2.50	27.75	27.7	19.17	19.00

TABLE XXX

Run 8. at 130°C, 20 psig, 0.07% Ni, and 1175 rpm

$k_{12} = 1.0$, $k_{13} = 0.0$, $k_{23} = 0.55$, $k_{24} = 0.0$, $k_{34} = 0.6$

95	36.60	36.60	31.99	31.70	4.56	4.95
90	31.35	31.35	34.46	34.30	6.20	7.20
80	22.20	22.00	36.76	36.40	12.10	11.80
70	14.35	14.35	35.75	36.65	15.85	15.75
60	7.70	8.15	33.80	35.35	17.52	18.85
50	2.45	3.40	23.15	33.20	22.10	20.00

TABLE XXXI

Run 10. at 130°C, 140 psig, 0.07% Ni, and 1175 rpm

$k_{12} = 0.65$, $k_{13} = 0.35$, $k_{23} = 0.12$, $k_{24} = 0.24$, $k_{34} = 0.4$

95	38.20	38.20	29.27	29.40	3.90	4.15
85	29.30	29.30	32.20	31.95	7.40	7.90
75	21.50	21.50	33.58	33.60	10.30	10.30
65	14.70	14.60	33.61	33.90	12.30	12.00
55	9.10	9.00	31.80	32.60	13.60	13.30
45	4.70	4.70	27.70	29.00	14.10	14.00
35	1.90	2.00	21.67	23.05	12.40	13.65

TABLE XXXII

Run 12. at 130°C, 60 psig, 0.07% Ni, and 550 rpm

$k_{12} = 1.0$, $k_{13} = 0.0$, $k_{23} = 0.46$, $k_{24} = 0.0$, $k_{34} = 0.33$

100	42.40	42.40	26.00	28.30	2.60	3.22
90	29.80	29.80	36.04	36.35	8.25	6.19
80	20.30	20.30	38.71	39.05	13.10	11.16
70	13.20	13.20	38.05	37.75	17.10	16.75
60	8.45	7.40	34.07	34.65	20.20	20.61
52.7	5.75	3.70	31.78	32.37	21.48	22.90

APPENDIX D

SEVENTEEN MECHANISMS PROPOSED FOR CATALYTIC HYDROGENATION

In the following proposed mechanisms:

K' = overall equilibrium constant for the hydrogenation reaction.

K = equilibrium constant for chemisorption (Subscript H refers to hydrogen, U to unsaturate, S to saturate, and I to inerts).

A = activity (Subscript H refers to hydrogen, U to unsaturate, S to saturate, and I to inerts).

B = kinetic term; it is different for each equation, but is constant for a given equation at a definite temperature.

Assumptions were made in applying the seventeen proposed mechanisms to the hydrogenation of cottonseed oil; these were as follows:

1. K' is large, so that all terms containing K' in the denominator can be considered zero.
2. A_U is proportional to the iodine value.
3. A_H is proportional to the hydrogen pressure.

PROPOSED MECHANISMS

I. Reaction between molecularly adsorbed hydrogen and adsorbed unsaturate:

(a) Adsorption of hydrogen controlling:

$$r = \frac{B}{1+A_UK_U+\frac{A_SK_H}{A_UK'}+A_SK_S+A_IK_I} \quad (A_H - \frac{A_S}{A_UK'})$$

See equation (43) page 921[27]

(b) Adsorption of unsaturate controlling:

$$r = \frac{B}{1+A_HK_H+\frac{A_SK_U}{A_HK'}+A_SK_S+A_IK_I} \quad (A_U - \frac{A_S}{A_HK'})$$

See equation (43) page 921[27]

(c) Desorption of saturate controlling:

$$r = \frac{B}{1+A_HK_H+A_UK_U+A_HA_UK'K_S+A_IK_I} \quad (A_HA_U - \frac{A_S}{K'})$$

See equation (44) page 921[27]

(d) Surface reaction reaction:

$$r = \frac{B}{(1+A_HK_H+A_UK_U+A_SK_S+A_IK_I)^2} \quad (A_HA_U - \frac{A_S}{K'})$$

See equation (42) page 920[27]

II. Reaction between atomically adsorbed hydrogen and adsorbed unsaturate:

(e) Adsorption of hydrogen controlling:

$$r = \frac{B}{(1+A_UK_U+\sqrt{\frac{A_SK_H}{A_UK'}}+A_SK_S+A_IK_I)^2}\left(A_H - \frac{A_S}{A_UK'}\right)$$

(f) Adsorption of unsaturate controlling:

$$r = \frac{B}{1+\sqrt{A_HK_H}+\frac{A_SK_U}{A_HK'}+A_SK_S+A_IK_I}\left(A_U - \frac{A_S}{A_HK'}\right)$$

(g) Desorption of saturate controlling:

$$r = \frac{B}{1+\sqrt{A_HK_H}+A_UK_U+A_HA_UK_SK'+A_IK_I}\ A_HA_U - \frac{A_S}{K'}$$

(h) Surface reaction controlling:

$$r = \frac{B}{(1+\sqrt{A_HK_H}+A_UK_U+A_SK_S+K_IA_I)^3}\ A_HA_U - \frac{A_S}{K'}$$

III. Reaction between unsaturate physically adsorbed (i.e., not chemisorbed) and molecularly adsorbed hydrogen:

(i) Adsorption of hydrogen controlling:

$$r = \frac{B}{1+\frac{A_SK_H}{A_UK'}+A_SK_S+A_IK_I}\left(A_H - \frac{A_S}{A_UK'}\right)$$

(j) Desorption of saturate controlling:

$$r = \frac{B}{1+A_H K_H + K' K_S A_H A_U + A_I K_I} \left(A_H A_U - \frac{A_S}{K'}\right)$$

(k) Surface reaction controlling:

$$r = \frac{B}{1+A_H K_H + A_S K_S + A_I K_I} \left(A_H A_U - \frac{A_S}{K'}\right)$$

IV. Reaction between unsaturate physically adsorbed (i.e., not chemisorbed) and atomically adsorbed hydrogen:

(l) Adsorption of hydrogen controlling:

$$r = \frac{B}{\left(1+\sqrt{\frac{A_S K_H}{A_U K'}} + A_S K_S + A_I K_I\right)^2} \left(A_H - \frac{A_S}{A_U K'}\right)$$

(m) Desorption of saturate controlling:

$$r = \frac{B}{1+\sqrt{A_H K_H} + K' K_S A_H A_U + A_I K_I} \left(A_H A_U - \frac{A_S}{K'}\right)$$

(n) Surface reaction controlling:

$$r = \frac{B}{\left(1+\sqrt{A_H K_H} + A_S K_S + A_I K_I\right)^2} \left(A_H A_U - \frac{A_S}{K'}\right)$$

V. Reaction between hydrogen in the fluid phase and adsorbed unsaturate:

(o) Impact of hydrogen upon adsorbed unsaturate:

$$r = \frac{B}{1+A_U K_U + A_S K_S + A_I K_I} \left(A_H A_U - \frac{A_S}{K'}\right)$$

(p) Desorption of saturate controlling:

$$r = \frac{B}{1+A_U K_U + K' K_S A_H A_U + A_I K_I} \left(A_H A_U - \frac{A_S}{K'}\right)$$

(q) Adsorption of unsaturate controlling:

$$r = \frac{B}{1+\frac{A_S K_U}{A_H K'} + A_S K_S + A_I K_I} \left(A_U - \frac{A_S}{A_H K'}\right)$$

BIBLIOGRAPHY

1. Bailey, A. E., Industrial Oil and Fat Products, Interscience Publishers, Inc., New York, 1951.

2. W. Norman, Brit. Pat. 1,515 (1903).

3. J. J. Burchenal, U. S. Pat. 1, 135, 351 (1915).

4. V. Mills (to Proctor and Gamble Co.), U. S. Pats. 2,520,422 to 2,522,425 (1950).

5. Bailey, A. E., Cottonseed, Interscience Publishers, Inc., New York, 1948.

6. Private Communications with the Werner G. Smith Company, Cleveland, Ohio (1952).

7. Brice, B. A., and Swain, M. L., J. Opt. Soc., 35, 532-44 (1945).

8. Moore, H. K., Richter, G. A., and Van Arsdel, W. B., Ind. Eng. Chem., 9, 451-62 (1917).

9. Richardson, A. S., Knuth, C. A., and Milligan, C. H., Ind. Eng. Chem., 16, 519-22 (1924).

10. Richardson, A. S., and Snoody, A. O., Ind. Eng. Chem., 18, 570-71 (1926).

11. Dhingra, D. R., Hilditch, T. P., and Rhead, A. J., J. Soc. Chem. Ind., 51, 195 T (1932).

12. Bailey, A. E., Feuge, R. O., and Smith, B. A., Oil & Soap, 19, 169-76 (1942).

13. Bailey, A. E. and Fisher, G. S., Oil & Soap, 23, 14-18 (1946).

14. Mitchell, J. H., Kraybill, H. R., and Zscheile, F. P., Ind. Eng. Chem. Anal. Ed., 15-13 (1943).

15. Fuson, R. C., and Snyder, H. R., Organic Chemistry, John Wiley and Sons, Inc., New York, 1942.

16. Swern, D., Knight, H. B., Shreve, O. D., and Heether, M. R., J. Am. Oil Chem. Soc., 27, 17-21 (1950).

17. Bailey, A. E., J. Am. Oil Chem. Soc. 26, 644-48 (1949).

18. Krane, H. G., The Study of Rate Factors in Liquid Phase Hydrogenation, Ph. D. thesis, Ohio State University, 1953.

19. Wynkoop, R., and Wilhelm, R. H., Chem. Eng. Progr., 46, 300-10 (1950).

20. Sussman, M. V., and Potter, C., Ind. Eng. Chem., 46, 457-65 (1954).

21. Tschernitz, J., Bornstein, S., Beckmann, R. B., and Hougen, O. A., Trans. Am. Inst. Chem. Engrs., 42, 883-903 (1946).

22. Am. Oil Chem. Soc., Official and Tentative Methods, Revised to January 1, p. 31-2, 44b-44f (1941).

23. O'Connor, R. T., Stansbury, M. F., Damare, H. G., and Stark Jr., S. M., J. Am. Oil Chem Soc., 29, 461-66 (1952).

24. Frost, A. A., and Pearson, R. O., Kinetics and Mechanism, John Wiley and Sons, Inc., New York, 1953.

25. Zimov'ev, A. A., J. Applied Chem. (U.S.S.R.) 22, 1253-62 (1949); C.A. 44, 3778 (1950).

26. Gol'danskii, V. I., and Elovich, S. Yu., J. Phys. Chem. (U.S.S.R.) 20, 1085-93 (1946); C.A. 41, 2973 (1947).

27. Hougen, O. A., and Watson, K. M., Chemical Process Principles, Vol. III, New York, John Wiley & Sons, 1948.